

THE
QUARTERLY
JOURNAL
OF
THE CHEMICAL SOCIETY
OF
LONDON.

Committee of Publication.

W. DE LA RUE, PH. D., F.R.S. | W. A. MILLER, M.D. F.R.S.
A. W. HOFMANN, LL.D. F.R.S. | LYON PLAYFAIR, C.B. F.R.S.

VOL. XI.

76956
13/11/99

LONDON:
HIPPOLYTE BAILLIERE, 219, REGENT STREET,
AND 290, BROADWAY, NEW YORK, U.S.
PARIS: J. B. BAILLIERE, RUE HAUTEFEUILLE,
MADRID: BAILLY BAILLIERE, CALLE DEL PRINCIPE.
1859:

LONDON:
PRINTED BY HARRISON AND SONS,
ST. MARTIN'S LANE, W.C.

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ERRATA.

PAGE	LINE.
28	15 from bottom, for “·922,” read “·962.”
29	13, 14 from top, for “chloride of calcium,” read “sulphate of copper.”
„	7 from bottom, after “substance,” insert “which.”
„	2 from bottom, for “3·21,” read “32·1.”
„	1 from bottom, for “6·53,” read “6·55.”
„	11, 15, 20 from top, for “glycol,” read “glycocol.”

THE
QUARTERLY JOURNAL
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I.—*Note on Rosolic Acid.*

BY DR. HUGO MÜLLER.

SOME years since, while working with phenyl-alcohol (carbolic acid) I made an attempt to prepare and purify this substance, by converting the so-called crude carbolic acid, as obtained from the Tar Works, into a lime-salt, and leaving this compound for some time exposed to the action of the air, with the view of removing any adhering liquid hydrocarbon, naphthalin, and also those impurities which cause carbolic acid to turn brown by keeping.

Latterly, while working in Mr. Warren De la Rue's laboratory, a larger quantity of this crude carbolate of lime was left for many months in a warm drying closet, and this circumstance having escaped my notice for some time, in consequence of other more pressing matters occupying my attention, I was astonished on again examining this carbolate of lime, to find the whole mass converted into a red substance, which, on treatment with water, gave a beautiful dark red solution; and not a trace of carbolic acid (phenyl-alcohol) could be extracted, either from the aqueous red solution or from the insoluble brown residue, the latter containing only carbonate of lime, a small quantity of caustic lime, and a dark brown resinous substance.

A few experiments made with the red aqueous solution, soon sufficed to show that it consisted principally of a substance discovered many years ago by Runge, and named by him Rosolic Acid.

This unexpected result, and the fact that this substance had not been observed, or at all events mentioned, since the time of its discovery, induced me to make a few experiments in order to complete the history of this interesting body, so far as my material would permit, the more especially as several chemists have expressed doubts as to the existence of this beautiful compound.

After having tried Runge's method for the extraction of rosolic acid, it was found to be preferable to exhaust the crude material mentioned above with a very dilute and boiling solution of carbonate of ammonia, and to evaporate the so-obtained crimson solution nearly to dryness. During this operation, ammonia is given off, the crimson colour changing gradually to a yellowish red, and a dark resinous substance separates at the same time.

This resinous substance is the crude rosolic acid. In order to purify it, it was submitted to the following treatment proposed by Runge: the crude rosolic acid was dissolved in alcohol, and hydrate of lime added in slight excess; the beautiful crimson solution thus formed, was agitated for some time with the undissolved part of the lime, and then filtered; the filtrate diluted with water; and lastly, the alcohol distilled off. The residuary solution of rosolate of lime was then decomposed, with a just sufficient quantity of acetic acid, and the whole boiled until every trace of free acetic acid and still adhering alcohol was volatilised. The rosolic acid separated in the form of a bright red precipitate, which, on the application of heat, caked together, and after cooling, formed a dark brittle substance with a greenish metallic lustre. The object of this treatment is the removal of a substance also discovered by Runge, and called by him brunolic acid, which, when combined with lime, is insoluble in alcohol. To ensure, however a perfect separation of this latter substance from the rosolic acid, it was found necessary to repeat the above-mentioned treatment of the alcoholic solution with lime.

On incineration, the so-prepared rosolic acid was found to leave a considerable quantity of carbonate of lime. In order to get rid of the lime, it was again dissolved in alcohol, and a minute quantity of hydrochloric acid added; the alcoholic solution was then thrown into a large quantity of water, which precipitated the rosolic acid in a state of purity, and fit for analysis.

Pure rosolic acid, previously boiled with water, is a dark greenish, amorphous substance, which possesses in a high degree the greenish metallic lustre of cantharides. Its powder is of a bright red, and resembles very much a Brazilian dye-stuff called *carajuru*, recently investigated by Erdmann; like this substance, when pressed or rubbed with a hard and smooth body, it assumes a bright gold-like lustre, and during pulverization it becomes highly electric. In thin layers, rosolic acid is transparent, with a fine red tint; very thin films in transmitted light appear of a deep orange colour, and in reflected light, of a golden metallic lustre. When thrown down from an alcoholic solution with water, it forms a flocculent precipitate of a bright red colour, resembling basic chromate of lead.

At a temperature of about 60° C. (170° F.) it cakes together, and in boiling water melts to a heavy, dark green, almost black liquid. It is not volatile; when heated in a tube, it melts and gives off yellow fumes; but the principal part remains behind as a charred mass or coke, extremely difficult to burn on the platinum foil.

Alcohol and ether dissolve rosolic acid with great facility, forming brownish yellow solutions, which on evaporation leave the rosolic acid in an amorphous state. Carbolic acid and wood creosote likewise dissolve it with ease.

Concentrated acids, as acetic acid, hydrochloric and sulphuric acids, also readily dissolve rosolic acid; from the resulting brownish yellow solutions water precipitates the original substance in a flocculent state. Contrary to Runge's experience, I found that when in a state of purity, it is soluble to a certain extent even in cold water, forming a bright yellow solution; boiling water, however, dissolves it much more readily, and yields up the greater part on cooling, as a granular deposit of a remarkably bright red colour, approaching vermilion in brilliancy.

In chloroform, benzol, and sulphide of carbon, rosolic acid is insoluble.

Although the substance under consideration was originally denominated an acid by its discoverer, it must be remarked that its acid properties are so feebly manifested, that it is even a weaker acid than carbonic acid. It only combines with ammonia, the caustic alkalies and caustic earths; it forms with them dark red compounds, which dissolve with the most magnificent red colour in water and alcohol; but these compounds are so unstable that when exposed to the combined action of the air and sunlight, they are

soon decomposed, the carbonic acid of the air seizing the base. The prolonged action of light and air ultimately destroys the rosolic acid completely.

A solution of the lime-salt, when carefully evaporated over caustic lime in a vacuum, leaves the compound as a granular or crystalline powder, which when pressed resembles earthamine.

The only compound of rosolic acid which shows comparative stability is the magnesia-salt, most probably on account of the lesser affinity of this base for carbonic acid. The employment of caustic magnesia in the purification of rosolic acid has, therefore, advantages over that of lime.

No precipitates are formed with a solution of the rosolates with the acetate or basic acetates of lead, or with any other metallic salt, nor is it carried down as a lake, by alumina or any other metallic oxide.

It will be perceived that this behaviour is at variance with the statement made by Runge, according to which rosolic acid gives with certain mordants, red tints and lakes equal to those furnished by cochineal and madder.

However, even if this were the case, the extreme fugitiveness of rosolic acid precludes the hope of its application in the arts, although its compounds are of the most beautiful red colour, and its preparation on the large scale would not be attended with any difficulty.

Chlorine and bromine act readily upon rosolic acid, either when dissolved in alcohol or in an alkaline solution, forming a light yellow compound which no longer dissolves with red colour in caustic alkalies.

Nitric acid heated with rosolic acid, acts in a similar manner to chlorine and bromine.

A solution of grape-sugar in caustic potash has no effect upon rosolic acid.

The analysis of rosolic acid presents some difficulty, on account of the resistance it offers to burning; it is, therefore, necessary to use oxygen for its combustion,

I. 0.2025 grains substance, dried over sulphuric acid, gave 0.5669 carbonic acid, corresponding to 76.24 per cent. carbon; and 0.1073 water, corresponding to 5.88 per cent. hydrogen.

II. 0.1844 substance gave 0.5113 carbonic acid, corresponding to 75.61 per cent. carbon; and 0.0960 of water, corresponding to 5.78 per cent. hydrogen.

These results agree with the following empirical formula $C_{46}H_{22}O_8$ which requires:—

Theory.		Experiment.		
		I.	II.	Mean.
$C_{46} =$	276 76·27	76·24	75·61	75·92
$H_{22} =$	22 6·05	5·88	5·78	5·83
$O_8 =$	64 17·68			18·25
	<hr/> 362 100·00 <hr/>			<hr/> 100·00 <hr/>

There is, unfortunately, no compound of rosolic acid stable enough to serve for the determination of its true formula.

With regard to the formation of rosolic acid, I may mention that I attempted to isolate the substance which, in contact with air and caustic alkalis, gives rise to the formation of rosolic acid, but without result, probably on account of the small quantity present, and the similarity of its properties with those of carbolic acid. Most probably, the substance in question resembles pyrogallie acid and pyrocatechin, the latter being also found amongst the products of the distillation of wood.

I must also state that I never succeeded in detecting rosolic acid in the way Runge describes, readily formed in coal-tar oil or in carbolic acid of commerce, unless the substance had been previously exposed for a considerable length of time to the action of air and caustic alkali. The employment of lime for this purpose is, however, preferable on account of its porosity.

In concluding this note, I beg to express my best thanks to Mr. Warren de la Rue, in whose laboratory the preceding experiments were performed.

II.—*On the Arseniates of Baryta, Lime, and Magnesia, and the Separation of Arsenic from other Elements.*

BY FREDERICK FIELD, M.R.I.A., F.C.S.

ALL chemists must have experienced the difficulty of separating arsenic from other elements with which it is associated. It is scarcely necessary to say that the method usually adopted, is to precipitate the arsenic as sulphide with the other metals which are thrown down by sulphide of hydrogen from their acid solutions, and subsequently digest the precipitate with the sulphides of ammonium or potassium. Many other bodies, however, are re-dissolved as well as the sulphide of arsenic, the separation of which in this stage of the process becomes exceedingly perplexing and difficult. Even in the earlier operations of the analysis, the arsenic has to be entirely converted from arsenic acid into arsenious acid, in order to insure its entire precipitation, and this is usually effected by sulphurous acid or a sulphite. When the arsenic exists in a very large proportion, repeated deoxidations and precipitations are necessary, which not only involve the expenditure of much time and labour, but are attended with loss of the substance under analysis. Much of the arsenic, it is true, can be eliminated by calcination, with occasional additions of carbon; and probably in the establishments where nickel and cobalt are obtained on a large scale, eight or nine-tenths of the arsenic are got rid of by this method. Even then the manipulator finds it necessary to pass a powerful and long-continued stream of sulphuretted hydrogen through the solution of the oxides, and to expel the excess by ebullition, previous to the separation of iron, nickel, and cobalt. Calcination, however, is inadmissible in chemical analysis, for—independently of the mechanical loss which is likely to occur—some metals, especially silver, are volatile in arsenical fumes. Moreover, presuming that all the operations mentioned above, have been carried out successfully, the arsenic cannot be separated entirely by the alkaline sulphides. Mr. Bloxam has shown* that when the proportion of copper is large,

* Quarterly Journal of the Chemical Society, vol. v, p. 104.

much arsenic is left with its sulphide, even after long digestion with sulphide of ammonium, and indeed that 1 per cent. of arsenic becomes insoluble in the alkaline sulphide, when the remainder consists of sulphide of copper. In the analysis of the ores of nickel and cobalt, I have found the formation of arseniate of potash highly useful, as a means of separating arsenic from these metals. When the arseniates of nickel and cobalt, in solution of hydrochloric acid, are boiled with excess of potash, they are entirely decomposed, the whole of the arsenic acid uniting with the alkali. Ammonia cannot be employed, as the arseniate of nickel is very slowly decomposed by this reagent. When native arseniate of nickel is dissolved in hydrochloric acid, and ammonia added, a gelatinous white precipitate is produced, and the supernatant liquid is colourless; and in order to obtain the blue ammoniacal solution, it is first necessary to free the nickel from arsenic. Iron is also present in this class of minerals, and sesqui-arseniate of iron is highly soluble in ammonia, so that if the substance contain arsenic, it is impossible to separate nickel from iron by that alkali. When an arsenical ore of cobalt (containing iron) is digested in nitro-hydrochloric acid, and ammonia added in excess, no precipitate is formed, provided there be sufficient arsenic to convert the whole of the iron into arseniate, and chloride of ammonium to form a soluble compound with cobalt. The solution has a fine brown colour, and is decomposed by sulphate of magnesia, sesquioxide of iron and ammonio-arseniate of magnesia being formed. When only iron and arsenic are present, both are precipitated in this manner, and the supernatant liquid contains merely ammoniacal salts.

The employment of sulphate of magnesia in conjunction with ammonia, for the determination of arsenic acid, has been proposed by Levöl;* and Rose, in his Handbook of quantitative analysis, strongly recommends this process as very accurate, provided certain precautions are adopted in preparing the arseniate of magnesia and ammonia for the determination of its weight. Rose also applies this method to the separation of arsenic from antimony, and states that it is the best process known, furnishing very accurate results, if conducted with care.

I was led in the first instance, without previous acquaintance with the results of Levöl and Rose, to institute experiments with a view to the application of magnesia to the determination

* Ann. Ch. Phys., [3] xvii, 501.

of arsenic in the above manner, and to submit to a comparative examination the precipitates produced by baryta, lime, and magnesia in an ammoniacal solution of arsenic acid, for the purpose of ascertaining the relative values of the alkaline earths in this branch of analysis. The present communication contains a summary of these experiments.

Arseniate of Baryta.—When chloride of barium is added to a solution of arsenic acid in ammonia, the latter being in excess, a copious precipitate of trisarseniate of baryta is formed, consisting of $3\text{BaO}, \text{AsO}_5$. According to Graham, this substance attracts a small quantity of carbonic acid from the air. Berzelius says it is very slightly soluble in water, somewhat more soluble in aqueous ammonia; and Laugier informs us that the solubility does not seem to be increased by the presence of ammonia, potash or soda salts.* My own experiments differ considerably from the above.

The arseniate of baryta was found to consist, after very careful analysis, of—

Baryta . .	66·39
Arsenic Acid	33·32
	<hr/>
	99·71

or, $3\text{BaO}, \text{AsO}_5$

	Calculated.
3BaO . .	66·65
Arsenic Acid	33·35
	<hr/>
	100·00

The baryta was precipitated from the solution of the arseniate in hydrochloric acid, by sulphate of soda. After deoxidation by sulphurous acid, the arsenic was estimated as tersulphide—

10·00 grs. $3\text{BaO}, \text{AsO}_5 = 6·639 \text{ BaO}$ and $3·55 \text{ AsS}_3 = 3·33 \text{ AsO}_5$.

10·00 grs. arsenious acid were converted into arsenic acid, and ammonia added in excess. The addition of chloride of barium caused a precipitate, which, after washing with weak ammonia, until no chlorine could be detected in the filtrate, gave on desiccation at 300° Fahr. —

34·52 grs. $3\text{BaO}, \text{AsO}_5$. 34·57 grs. $3\text{BaO}, \text{AsO}_5$. Calculated.

Arseniate of baryta loses all its water at a temperature a little above 212° . After drying in a water-bath for several hours, 18·90 grs. only lost 0·05 on ignition. After drying upon a sand-

* Gmelin's Handbook, vol. iv, 304.

bath, at a temperature which never exceeded 300° , in a platinum crucible, no loss was experienced on heating to redness.

With regard to the solubility of this salt, the following experiments were performed :

10.00 grs. $3\text{BaO}, \text{AsO}_5$ digested with 2000 grs. cold distilled water for forty-eight hours, lost 1.10 gr. The filtrate gave 0.9 gr. sulphate of baryta on addition of sulphate of baryta.

10.00 id. digested with 2000 grs. solution of chloride of ammonium (containing 100 grs. of the dry salt) lost 3.852. The filtrate gave 3.41 sulphate of baryta.

10.00 id. digested with solution of ammonia formed by adding 200 grs. ammonia, sp. gr. .880, to 1800 grs. water, lost 0.06.

Sulphate of soda hardly produced any precipitate of sulphate of baryta in the filtrate.

From this it appears, that, although very soluble in chloride of ammonium, and moderately so in water, arseniate of baryta is very insoluble in aqueous ammonia. And even (as in most cases in analysis) when chloride of ammonium is present, the addition of excess of ammonia prevents in a great measure the solubility of the baryta salt. And it may be mentioned here, that ammonia determines the insolubility both of the magnesia and lime arseniates in the same manner, precipitating the ammonio-arsenates from their solution in chloride of ammonium. Chloride of barium can be advantageously employed for the detection of small quantities of arsenic acid, when in combination with copper and other metals.

100.00 grs. of copper free from sulphur were placed in a flask, together with 0.20 grs. arsenious acid. After solution in nitric acid, and addition of excess of ammonia, sulphate of magnesia caused a precipitate, which settled at the bottom of the vessel after 12 hours. On filtering the small precipitate, arsenic was readily detected by the usual test.

Minerals containing sulphur arsenic and nickel, can be very neatly and correctly analysed by the employment of a baryta salt. By adding chloride of barium in excess to the acid solution, sulphate of baryta is precipitated, and after filtration and addition of a large excess of ammonia, all the arsenic is precipitated, provided sufficient chloride of barium has been employed. It is necessary to add this reagent to the acid solution, and therefore to decompose the arseniate of nickel in hydrochloric acid. There is no fear of any nickel remaining with the

arseniate of baryta, which is a dense white powder, and can be thoroughly and expeditiously washed. For this purpose, of course a weak solution of ammonia is employed, instead of pure water.

Arseniate of Lime and Ammonia.—When diarseniate of ammonia, potash, or soda is added to a solution of chloride of calcium, trisarseniate of lime is formed, and the supernatant liquid becomes acid.

When chloride of ammonium, trisarseniate of ammonia, and lime-water are mixed together, crystals of arseniate of ammonia and lime $2\text{CaO}, \text{NH}_4\text{O}, \text{AsO}_5$ are found.* I have met with two distinct precipitates during the course of my experiments, which possessed the following characteristics:

10·00 grs. arsenious acid were converted into arsenic acid, ammonia added in very slight excess, and subsequently solution of chloride of calcium. The precipitate, after prolonged washing with water and dessication at 300° , weighed 15·50 grs., and on ignition lost only 0·80 gr., yielding 14·70 of a compound of arsenic acid and lime. A large quantity of arsenic was detected in the filtrate.

10·00 grs. of arsenious acid were similarly treated, and the precipitate washed with weak ammonia; after drying at 300° , it was found to weigh 18·24 grains, and 17·02 on ignition. The precipitates in both instances seemed to consist of different substances, one of a very slightly crystalline powder, the other of tolerably large needles, united together in stellated masses. Although in the latter experiment the 10 grs. of arsenious acid yielded 17·02 of lime salt, and by calculation it should yield 17·10 diarseniate of lime ($2\text{CaO}, \text{AsO}_5$) the loss by ignition was so small, and so much less than it would have been, had an atom of ammonia been expelled, as to lead me to doubt very much if the precipitate were the arseniate of lime and ammonia, notwithstanding that it evolved much ammonia on ebullition with potash.

In order to analyze the residue left upon ignition, advantage was taken of the fact, that arseniate of lime is perfectly decomposed by a boiling solution of oxalate of ammonia.

It is better, however, to dissolve the arseniate in hydrochloric acid, add the oxalate, and finally excess of ammonia, and boil for some time. The whole of the arseniate is found in the filtrate, and the lime in the precipitate as oxalate of lime.

The 14·70 grains boiled in this manner gave, on ignition, 8·00 carbonate of lime = 5·48 lime, and the 17·02 grs. gave

* Gmelin's Handbook, vol. iv, p. 304.

11.56 $\text{CaO}, \text{CO}_2 = 6.47 \text{ CaO}$. Sulphate of magnesia was added to the filtrate, and after standing some time, the ammonio-magnesian arseniate collected, and the arsenic estimated.

Composition of Diarsenate of Lime,

2CaO, AsO ₅ Calculated.			Lime Salt Found.		
Lime	.	4.82	Lime	.	5.48
Arsenic Acid		9.88	Arsenic Acid		9.27
		<hr/>			<hr/>
		14.70			14.75
Lime	.	5.57	Lime	.	6.47
Arsenic Acid		11.45	Arsenic Acid		10.44
		<hr/>			<hr/>
		17.02			16.91

It is evident from the above analyses, that the salt under consideration is not diarsenate of lime, but probably a mixture of diarsenate and triarsenate, the former produced by the decomposition of the ammonia compound, thrown down from the original solution in company with the triarsenate. The loss by ignition, as well as the quantities found of arsenic acid and lime leave no doubt that this is the case.

$3\text{CaO}, \text{AsO}_5 + 2\text{CaO}, \text{NH}_4\text{O}, \text{AsO}_5$, upon ignition $= 3\text{CaO}, \text{AsO}_5 + 2\text{CaO}, \text{AsO}_5$.

And the relative numbers are as follows:

				Found.
As	396	:	370	:: 18.24 : 17.04 .. 17.02
,,	396	:	370	:: 15.50 : 14.47 .. 14.70

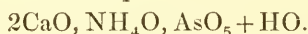
And with regard to the quantities of lime and arsenic acid:

$3\text{CaO}, \text{AsO}_5 + 2\text{CaO}, \text{AsO}_5$,

Calculated.		Found.	
Lime	. . 5.56	Lime	. . 5.48
Arsenic Acid	9.14	Arsenic Acid	9.27
	<hr/>		<hr/>
	14.70		14.75
Lime	. . 6.44	Lime	. . 6.47
Arsenic Acid	10.58	Arsenic Acid	10.44
	<hr/>		<hr/>
	17.02		16.91

It is not at all surprising that when ammonia is not in great excess, that trisarsenate of lime should be formed, as even diarsenate of ammonia produces this compound. It is, however, rather singular, that, when in combination with the diarsenate of lime, the trisarsenate does not lose arsenic acid upon ignition, which it does when heated *per se*.*

The arseniate of lime and ammonia can be readily formed by adding ammonia and trisarsenate of ammonia to a solution of chloride of calcium. The precipitants must be in considerable excess. This salt crystallises from weak solutions in large needle-shaped crystals, and from more concentrated solutions, it separates as a white crystalline mass. Like the baryta compound, it is more soluble in water than in aqueous ammonia, and soluble to a great extent in chloride of ammonium. It retains an atom of water at 212° , and consists at that temperature of



10.00 grs.	in 2000.00	grs. water,	lost 0.40 grs.
10.00 grs.	„	„	grs. weak ammonia, lost 0.02 grs.
10.00 grs.	„	„	grs. chloride of ammonium, containing 100 grs. dry salt, lost 8.300.†

This salt loses its atom of water at a temperature a little beyond 212° .

Dried at 280° .		Found.	Calculated.
18.25	on ignition gave	15.80	15.83
11.90	„ „	10.25	10.32
13.20	„ „	11.48	11.45

The residues were analysed separately, and found to consist of $2\text{CaO}, \text{AsO}_5$, as the following numbers will show :—

Calculated.	Found.
Lime . . . 5.18	5.01
Arsenic Acid 10.62	10.49
<hr/> 15.80	<hr/> 15.50

* The cold solution of this salt in chloride of ammonium, evolves ammonia copiously on ebullition, with formation of diarsenate of lime, which still remains dissolved in the liquid. According to Wach, diarsenate of lime when in solution of ammoniacal salts, becomes converted into arseniate of lime and ammonia, but this is decomposed on boiling with a re-formation of diarsenate of lime.

† The trisarsenate of lime is decomposed when ignited alone (Simon), Gmelin's Handbook, vol. iv, p. 304.

Calculated.			Found.
Lime	. .	3.41	3.38
Arsenic Acid		6.84	6.75
<hr/>			<hr/>
		10.25	10.13
Lime	. .	3.76	3.64
Arsenic Acid		7.72	7.69
<hr/>			<hr/>
		11.48	11.33

Arseniate of Magnesia and Ammonia.—This salt is thrown down in great purity, when arseniate of ammonia and excess of ammonia are added to a soluble salt of magnesia.

In applying this salt to the estimation of arsenic, Levöl recommends its ignition, and the determination of the arsenic as pyro-arseniate of magnesia ($2\text{MgO}, \text{AsO}_5$). But Rose has shown that a portion of arsenic acid is reduced, at a high temperature by ammonia, and volatilised, so that a loss in weight due to that reaction, is sustained in proportion to the necessary duration of the ignition. It is stated by the latter chemist that the weight of the double salt may be determined either by its desiccation *in vacuo*, in which case its composition is represented by the formula $2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + 12\text{HO}$, or at 212°F ., when it consists of—



Like the corresponding lime salt, it loses its water at a slight increase of temperature; at 180°F . it retains three atoms of water, and it loses its ammonia between 500° and 600° .

Its formula may be expressed at various temperatures, as follows :—

When dried <i>in vacuo</i> ,	$2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + 12\text{HO}.$
From 180° to 200°	$2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + 3\text{HO}.$
At 212° ..	$2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + \text{HO}.$
At 300° ..	$2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5.$
At 600° ..	$2\text{MgO}, \text{AsO}_5.$

In the estimation of arsenic from this compound, it is therefore very necessary to be extremely cautious in its desiccation. Specimens dried upon a filter placed above a sand-bath, with a thermometer suspended at the same distance from the heated surface (the mercury never rising above 300°), were found to have lost the whole of their water in from four to five hours.

The following experiments were tried regarding the solubility of this double salt :—

10·00 grs.	digested with	2000 grs. water,	lost	0·28 grs.
10·00	„ „ „	ammonia „		0·14 grs.
10·00	„ „ „	NH ₄ Cl „		1·90 grs.

Ammonia precipitates the salt from its solution in chloride of ammonium.

The following diagram will give, in a tabular form, the solubility of the arseniates of lime and ammonia, magnesia and ammonia, and arseniate of baryta, in water, ammonia, and chloride of ammonium.

	10 grs. 2MgO, NH ₄ O, AsO ₅ , HO.			10 grs. 2CaO, NH ₄ O, AsO ₅ , HO.			10 grs. 3BaO, AsO ₅ .		
Water	2000	..	0·28	2000	..	0·40	2000	..	1·10
Ammonia...	2000	..	0·14	2000	..	0·02	2000	..	0·06
Chloride of Ammonium	2000	..	1·90	2000	..	8·30	2000	..	3·85

From the foregoing experiments, the relative advantages and disadvantages in the employment of the salts of the alkaline earths may be estimated, and—

1. The precipitation of arsenic acid by a soluble salt of lime.

This is disadvantageous when sulphuric acid is present in the liquid. Sulphate of lime would be precipitated, and require long and protracted washing for its entire separation. Neither could the arseniates be freed from the sulphate by dilute hydrochloric acid, as the latter is especially soluble in that menstruum. Another objection is, the uncertainty of the compound precipitated, which would render its analysis indispensable when the *quantity* of arsenic, as well as its abstraction from other bodies, is desired. On the other hand, its great insolubility in ammonia, renders the employment of a lime-salt, in certain circumstances, very advantageous.

2. The employment of a soluble baryta salt. The objection regarding the sulphuric acid, cannot be urged, as in the case of the lime-salt. Sulphate of baryta is easily separated from its arseniate, and indeed the whole of the sulphuric acid could be

removed by chloride of barium, previously to the introduction of the ammonia. When chloride of ammonium does not exist in any very great quantity in the solution, the employment of baryta may be resorted to advantageously.

3. By a magnesia salt. Magnesia possesses many advantages over lime and baryta, which can be easily appreciated in practice. The ammonia-magnesian arseniate, after standing some hours, settles down in a heavy crystalline mass, so hard and dense, that the supernatant liquid may be frequently decanted off, and the crystals drained, thus rendering the subsequent washing very expeditious and easy. There is no fear of sulphuric acid being in the precipitate, which possesses the advantage of being very definite in composition, and insoluble in weak ammonia. From my own experience I should recommend magnesia above baryta and lime, if it were only for the greater facility of its management in chemical analysis.

The following estimations were invariably made with a magnesian salt :—

10.00 gr. arsenious acid converted into arsenic acid, and precipitated with a magnesian salt, gave $18.87 \text{ } 2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + \text{HO}$. Calculation 19.19.

10.00 gr. gave 18.94.

10.00 gr. AsO_3 , and 1 gr. copper dissolved in nitric acid, gave $19.14 \text{ } 2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + \text{HO} = 9.97 \text{ AsO}_3$.

1.00 gr. $\text{AsO}_3 + 10.00 \text{ gr. Cu}$, gave $1.90 \text{ } 2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + \text{HO}$; and when 0.19 gr. $\text{AsO}_3 = 0.076$ arsenic was boiled with NO_5 , and 100.00 of copper, a crystalline deposit of the ammonia-magnesian arseniate was observed on the sides of the flasks, after standing for 24 hours. On drawing off the copper and washing the crystals with weak ammonia, they were dissolved in HCl , and a clear yellow pentasulphide of arsenic obtained, on addition of a few drops of sulphide of ammonium, and afterwards, excess of hydrochloric acid.

It has been before observed that nickel can be easily and perfectly separated from arsenic by the introduction of a magnesian salt. In the following experiments, with a given weight of ore (?), the arsenic was not estimated, as the ore contained iron which was precipitated with the ammonio-magnesian arseniates.

The filtrate was precipitated by sulphide of ammonium, the sulphide dissolved, and the nickel thrown down as oxide by potash.

The first experiment	gave	..	6.127	oxide of nickel.
second	„	„	6.00	„
third	„	„	5.95	„

The Separation of Arsenic from Antimony by means of a soluble magnesian salt in the presence of ammonia, is very strongly recommended by Rose; and my own experiments fully confirm the statements of that chemist. The method described in detail in his Handbook succeeds perfectly; I may state, however, that as the tartaric acid, added to the solution of the oxidised metals for the purpose of retaining the antimony in solution, is sometimes liable to occasion the separation, with the arseniate, of a small quantity of tartrate of magnesia and ammonia, I have found it advisable to substitute sulphate of ammonia for the chloride of ammonium added previous to the ammonia. The double tartrate is very readily soluble, and the double arseniate particularly insoluble in the sulphate of ammonia.

The following analyses will show the correctness of the method :—

Taken.		Found.	
Arsenious Acid	5.00	$2\text{MgO}, \text{NH}_4\text{O}, \text{AsO}_5 + \text{HO}$	$9.54 = 4.97 \text{AsO}_3$.
Antimony	5.00		
Arsenious Acid	5.00	„	$9.52 = 4.95 \text{AsO}_3$.
Antimony	5.00		

The antimony was not determined in the above analyses; in those below, the arsenic was estimated as before, sulphide of ammonium added in excess to the filtrate, until the sulphide of antimony was completely re-dissolved. It was afterwards precipitated by hydrochloric acid. The precipitate was dried at 212° , weighed, and a portion examined quantitatively for sulphur, the weight of which was deducted, and the quantity calculated from the whole precipitate.

Taken.		Found.	
Arsenious Acid	. 10.00 = Arsenic	7.57 ..	7.39
Antimony	. . . =	6.80 ..	7.04
		<hr/>	<hr/>
		14.37	14.43
Arsenious Acid	. 12.40 = Arsenic	9.39 ..	9.12
Antimony	. . . =	12.40 ..	12.23
		<hr/>	<hr/>
		21.79	21.35

	Taken.			Found.
Arsenious Acid	1·00	.	= Arsenic 0·75	.. 0·68
Antimony	.	.	= 10·00	.. 9·89
			<hr/> 10·75	<hr/> 10·57
Arsenious Acid	10·00	.	= Arsenic 7·57	.. 7·42
Antimony	.	.	= 1·00	.. 0·98
			<hr/> 8·57	<hr/> 8·40

Arsenious Acid 0·10 } gave a crystalline precipitate of
 Antimony . 5·00 } $2\text{MgO}, \text{N H}_4\text{O}, \text{AsO}_5 + \text{HO}$ on the
 sides of the glass.

Arsenious Acid 5·00 } filtrate gave an orange-red preci-
 Antimony . 0·10 } pitate of sulphide of antimony.

Arsenic cannot be separated from tin by means of magnesia. Ammonia produces no precipitate in the solution of the bichloride of tin when tartaric acid is present, but a precipitate is produced by the introduction of magnesian salts, which appears to contain both tin and magnesia, but which, so far as I know, has not been examined. Hopes may be entertained that antimony may be separated from tin by taking advantage of this fact.

The subject is now under consideration, and promises satisfactory results, though rather difficult and laborious.

III.—*On the existence of a Second Crystallizable Fluorescent Substance (Pavine) in the Bark of the Horse-Chestnut.*

By G. G. STOKES, M A., SEC. R. S., &c.

ON examining, a good while ago, infusions of the barks of various species of *Æsculus*, and the closely allied genus *Pavia*, I found that the remarkably strong fluorescence shown by the horse-chestnut ran through the whole family. The tint of the fluorescent light was, however, different in different cases, being as a general rule blue throughout the genus *Æsculus*, and a blue-green throughout *Pavia*. This alone rendered it evident, either that there were at least two fluorescent substances present, one in one bark and another in another, or, which appeared more probable, that

there were two (or possibly more) fluorescent substances present in different proportions in different barks.

On examining, under a deep violet glass, a freshly cut section of a young shoot, of at least two years' growth, of these various trees, the sap which oozed out from different parts of the bark or pith was found to emit a differently coloured fluorescent light. Hence, even the same bark must have contained more than one fluorescent substance; and as the existence of two would account for the fluorescent tints of the whole family, a family so closely allied botanically, the second of the suppositions mentioned above appeared by far the more probable.

I happened to put some small pieces of horse-chestnut bark with a little ether into a bottle, which was laid aside, imperfectly corked. On examining the bottle after some time, the ether was found to have evaporated, and had left behind a substance crystallized in delicate radiating crystals. This substance, which I will call paviin, when dissolved in water, yields, like *æsculin*, a highly fluorescent solution, and the fluorescence is in both cases destroyed (comparatively speaking) by acids, and restored by alkalies. The tint, however, of the fluorescent light is decidedly different from that given by pure *æsculin*, for a specimen of which I am indebted to the kindness of the Prince of Salm-Horstmar, being a blue-green in place of a sky-blue. The fluorescent tint of an infusion of horse-chestnut bark is intermediate between the two, but much nearer to *æsculin* than to paviin.

In all probability, the fluorescence of the infusions of barks from the closely allied genera *Æsculus* and *Pavia*, is due to *æsculin* and paviin present in different proportions, *æsculin* predominating generally in the genus *Æsculus*, and paviin in *Pavia*.

Æsculin and paviin are extremely similar in their properties, so far as they have yet been observed. They are most easily distinguished by the different colour of the fluorescent light of their solutions, a character which is especially trustworthy, as it does not require for its observation that the solutions should be pure. Paviin, as appears from the way in which it was first obtained, must be much more soluble than *æsculin* in ether. *Æsculin* is indeed described as insoluble in ether, but it is sufficiently soluble to render the ether fluorescent. Paviin, like *æsculin*, is withdrawn from its ethereal solution by agitation with water. Though of feeble affinities, it is rather more disposed than *æsculin* to combine with oxide of lead. If a decoction of horse-chestnut bark be

purified by adding a sufficient quantity of a salt of peroxide of iron or of alumina, precipitating by ammonia, and filtering, and the ammoniacal filtrate be partially precipitated by very dilute acetate of lead, the whole redissolved by acetic acid, reprecipitated by ammonia, and filtered, the fluorescent tint of the filtrate will be found to be a deeper blue than that of the original solution; while, if the fluorescent substances combined with oxide of lead (the compound itself is not fluorescent) be again obtained in alkaline solution, the tint, as compared with the original, will be found to verge towards green. The required solution is most easily obtained from the lead-compounds by means of an alkaline bicarbonate, which plays the double part of an acid and an alkali, yielding carbonic acid to the oxide of lead, and ensuring the alkalinity of the filtrate from carbonate of lead. It is very easy in this way, by repeating the process, if necessary, on the filtrate from the first precipitate, to obtain a solution which will serve as a standard for the fluorescent tint of pure *æsculin*. A solution, serving nearly enough as a standard of comparison in this respect for pure *paviiu*, may be had by making a decoction of a little ash bark, adding a considerable quantity of a salt of alumina, precipitating by ammonia, and filtering. By partial precipitation in the manner explained, it is very easy to prove a mixture of *æsculin* and *paviiu* to be a mixture, even when operating on extremely small quantities.

It must be carefully borne in mind, that the characteristic fluorescent tint of a solution is that of the fluorescent light coming from the solution *directly* to the eye. Even should a solution of the pure substance be nearly colourless by transmitted light, though strong enough to develop the fluorescence to perfection, if the solution be impure it is liable to be coloured, most commonly yellow of some kind, which would make a blue seen through it appear green. To depend upon the fluorescent tint, as seen through and modified by a coloured solution, would be like depending on the analysis, not of the substance to be investigated, but of a mixture containing it. Yet in solutions obtained from the horse-chestnut, and in similar cases, the true fluorescent tint can be observed very well, in spite of considerable colour in the solution.

The best method of observing the true fluorescent tint is to dilute the fluid greatly, and to pass into it a beam of sunlight, condensed by a lens fixed in a board, in such a manner that as

small a thickness of the fluid as may be shall intervene between the fluorescent beam and the eye. If a stratum of this thickness of the dilute solution be sensibly colourless, the tint of the fluorescent light will not be sensibly modified by subsequent absorption. This, however, requires sunlight, which is not always to be had. Another excellent method, requiring only daylight, and capable of practically superseding the former in the examination of horse-chestnut bark, is the following, in using which it is best that the solutions should be pretty strong, or at least not extremely dilute.

A glass vessel with water is placed at a window, the vessel being blackened internally at the bottom by sinking a piece of black cloth or velvet in the water, or otherwise. The solutions to be compared as to their fluorescent tint are placed in two test tubes, which are held nearly vertically in the water, their tops slightly inclining from the window, and the observer regards the fluorescent light from above, looking outside the test tubes. Since by far the greater part of the fluorescent light comes from a very thin stratum of fluid next the surface by which the light enters, the fluorescent rays have mostly to traverse only a very small thickness of the coloured fluid before reaching the eye; the water permits the escape of those fluorescent rays which would otherwise be internally reflected at the external surface of the test tubes; and the intensity of the light of which the tint is to be observed is increased by foreshortening. The observer would do well to practice with a fluorescent fluid purposely made yellow by introducing some non-fluorescent indifferent substance; thus, a portion of the standard solution of *æsculin* mentioned above may be rendered yellow by ferrid-cyanide of potassium. The more completely the fluorescent tints of the yellow and the nearly colourless solution agree, the more nearly perfect is the method of observation. If ferro-cyanide of potassium be used in the experiment suggested, instead of ferridcyanide, the most marked effect is a diminution in the intensity of the fluorescent light, the cause of which is that the absorption by this salt takes place more upon the active, or fluorogenic, than upon the fluorescent rays. Since substances of a similar character may be present in an impure solution, the observer must not always infer poverty with regard to fluorescent substances from a want of brilliancy in the fluorescent light.

The existence of pavin may perhaps account for the discrepancies between the analyses of *æsculin* given by different chemists.

I should mention, however, that I have met with three specimens of æsculin, and they all appeared to be free from paviin. The reason why æsculin was obtained pure from a decoction containing paviin also, is probably that the former greatly preponderates over the latter in the bark of the horse-chestnut. A decoction of this bark yielded to me a copious crop of crystals of æsculin, while the paviin, together with a quantity of æsculin still apparently in excess, remained in the mother liquor. I may, perhaps, on some future occasion communicate to the Society the method employed, when I have leisure to examine it further; I will merely state for the present that it enabled me to obtain crystallized æsculin in a few hours, without employing any other solvent than water. In the method commonly employed, the first crystallization of æsculin is described as requiring some fourteen days.

On account of the small quantity, apparently, of paviin, as compared with æsculin, present in the bark of the horse-chestnut, a chemist who wished to obtain the substance for analysis would probably do well to examine a bark from the genus *Pavia*, if such could be procured. The richness of the bark in paviin, as compared with æsculin, may be judged of by boiling a small portion with water in a test tube; those barks in which the substance presumed to be paviin abounds yield a decoction having almost exactly the same fluorescent tint as that of a decoction of ash bark.

A crystallizable substance, giving a highly fluorescent solution, has been discovered in the bark of the ash, by the Prince of Salm-Horstmar,* who has favoured me with a specimen. This substance, which has been named *fraxin* by its discoverer, is so similar in its optical characters to paviin that the two can hardly, if at all, be distinguished thereby; but as *fraxin* is stated to be insoluble in ether, it can hardly be identical with paviin, which was left in a crystallized state by that solvent. I find, however, that *fraxin* is sufficiently soluble in ether to render the fluid fluorescent, so that after all it is only a question of degree, which, cannot be satisfactorily settled till paviin shall have been prepared in greater quantity.

* Poggendorff's *Annalen*, vol. 100 (1857), p. 607.

IV.—On the Action of Bromine on Acetic Acid.

By W. H. PERKIN, F.C.S., AND B. F. DUPPA, Esq.

SINCE the publication of the notice which appeared in the "Philosophical Magazine" last September, we have studied some of the reactions of bromacetic acid on various substances, and have also succeeded in obtaining bibromacetic acid. We shall first describe the method pursued in making these interesting substances.

Bromacetic Acid.

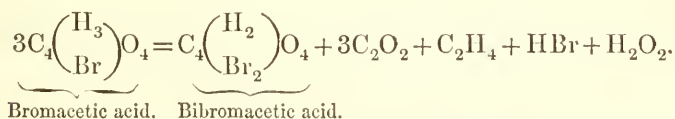
The best method of preparing this substance is to take a mixture of crystallizable acetic acid and bromine, in the proportion of one equivalent of bromine to one of acid, the object of the excess of acetic acid being to absorb the hydrobromic acid gas, so as to relieve the tube of pressure, and introduce it into a strong sealed tube, which is then placed in an oil bath, and heated up to 150°C . As soon as this temperature has been reached, the bath may be allowed to cool down gradually; the cooling may occupy two hours or more. The mixture is then generally nearly colourless, or of a light amber-brown. The decolorization takes place very suddenly at about 146°C ., at which moment the tubes are apt to burst, though the bath may have been as high as 155°C . The tube, when quite cold, is opened, from which torrents of hydrobromic acid gas issue; the contents are then transferred to a retort, and a receiver being attached, together with proper apparatus for the condensation of the hydrobromic acid liberated, heat is applied, and the temperature raised until it reaches 200°C .* The retort is then left to cool, when after a time, the whole of the liquid contents become solid and beautifully crystalline. This is a mixture of hydrobromic, bromacetic, and bibromacetic acids. These mixed acids are then heated to 130°C ., and carbonic acid passed until the reaction of hydrobromic acid with nitrate of silver is no longer evident. Carbonate of lead in excess is then added, together with about ten times as much water in bulk as there is acid; the whole heated to 100°C ., and allowed to stand for some hours; the liquid filtered off from the crystalline deposit which has formed; the

* As a quantity of bromacetic acid is carried over long before 200°C . is reached, it is as well to re-distil the distillate. As an additional quantity of solid acid is thus procured, the liquid may again be used with bromine for the production of more acid.

crystals washed with a little cold water, and diffused in water; and sulphuretted hydrogen passed to saturation. The liquid filtered off and concentrated, yields the crystalline acid in a state of purity. The object of the last process is to separate the bromacetic acid from the bibromacetic acid, the lead salt of the latter being much more soluble than that of the former.

The acid thus obtained crystallizes in rhombohedra; it is exceedingly deliquescent, and very soluble in water or alcohol. It fuses below 100°C ., and boils at 208°C . When distilled with acetate of potassium, it gives off acetic acid; when heated with metallic zinc, it yields acetate and bromide of zinc.

It undergoes a singular change when exposed to a high temperature in a sealed tube, carbonic oxide, bibromacetic acid, and apparently a little hydride of methyl being formed; it is possible that the following reaction may take place:



It attacks the epidermis powerfully, raising a blister like that produced by a burn; the effect when the acid is diluted, takes place after eight or ten hours.

Bromacetic acid forms crystallizable salts with most of the bases, many of which decompose rapidly; few of these have been examined quantitatively.

Bromacetate of Ammonium is a nearly uncrystallizable salt, very soluble in water; when heated it decomposes, yielding bromide of ammonium.

Bromacetate of Potassium. This salt is obtained by neutralizing a solution of carbonate or hydrate of potassium with bromacetic acid, and evaporating the solution in a water bath. It is a crystalline salt very soluble in water and alcohol.

Bromacetate of Sodium is a very soluble salt, insoluble, or nearly so, in alcohol.

Bromacetate of Barium crystallizes with difficulty in small stars, and contains water of crystallization; it is tolerably soluble in alcohol.

Bromacetate of Calcium is a very difficultly crystallizable salt, and very soluble in water.

Bromacetate of Copper is a green crystalline salt, very soluble in

water. A solution of it appears to decompose when boiled, as the colour becomes paler. The solution after standing for some days, deposits needle-shaped crystals and small malachite-green tufts of great beauty. They appear to contain a large quantity of water of crystallization.

Bromacetate of Lead.—This salt is obtained, either by neutralizing bromacetic acid with oxide of lead, and recrystallizing the product in water, or by adding a solution of bromacetic acid to a solution of acetate of lead, washing the resulting crystalline precipitate with cold water, and then recrystallizing from water.

A specimen dried at 100° C., when burnt with chromate of lead, gave the following numbers :

·9880 of Bromacetate of Lead gave
·3717 of Carbonic Acid and
·0830 of Water.

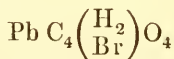
A determination of lead and bromine gave the following numbers :

·674 of Bromacetate of Lead gave
·3106 of Oxide of Lead, and
·5244 of Bromide of Silver.

These numbers lead to the following percentage composition :

Carbon	10·25
Hydrogen	0·92
Bromine	33·10
Lead	42·774

The formula



requires the following numbers :

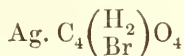
	Theory.		Exp.
4 equiv. of Carbon	= 24·00	9·930	10·25
2 equiv. of Hydrogen	= 2·00	0·820	·92
1 equiv. of Bromine	= 79·97	33·117	33·10
1 equiv. of Lead	= 103·57	42·878	42·774
4 equiv. of Oxygen	= 32·00	13·255	
	<hr/>	<hr/>	
	241·54	100·000	

Bromacetate of lead crystallizes in needles, is difficultly soluble in cold, but moderately so in hot water.

Bromacetate of Silver is obtained by treating bromacetic acid with carbonate of silver, or by adding a solution of bromacetic acid to a solution of nitrate of silver. In the latter case it is thrown down as a beautiful crystalline precipitate, which is washed with cold water, and dried over sulphuric acid in vacuo. A determination of the silver gave the subjoined number :

·6500 of Bromacetate of Silver gave
·4935 of Bromide of Silver, or
43·617 per cent. of Silver.

The formula



requires 43·9 per cent. of silver.

This salt is very unstable, decomposing by ebullition, bromide of silver and an acid which we shall refer to hereafter, being formed. The dry salt, if heated to about 90° C., decomposes with a sort of an explosion. It is rapidly acted upon by light when moist.

Bromacetate of Methyl.—This substance is obtained by heating a mixture of hydrate of methyl and bromacetic acid in a sealed tube for an hour, to a temperature of 100° C., washing the product with water, drying over chloride of calcium, and rectifying.

Bromacetate of methyl is a clear colourless mobile liquid, having an aromatic odour highly irritating both to the nose and the eyes. It is heavier than water; it boils at about 144° C., decomposing gradually every time it is distilled. Ammonia acts on it very readily.

Bromacetate of Ethyl is obtained in the same way as the preceding, substituting hydrate of ethyl for that of methyl. It is a clear colourless liquid, heavier than water, and highly irritating to the eyes and nose. It boils at 159° C.

A combustion with chromate of lead yielded the following numbers :

0·3821 of substance gave
0·3922 of Carbonic Acid and
0·1215 of Water.

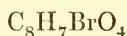
A determination of bromine gave the following numbers :

0.4942 substance gave
0.5110 of Bromide of Silver.

These numbers give the following percentage composition :

Carbon	27.976
Hydrogen	3.533
Bromine	47.53

The formula



requires the following numbers :

	Theory.		Exp.
8 equiv. of Carbon	48.00	28.70	27.976
7 equiv. of Hydrogen	7.00	4.18	3.533
1 equiv. of Bromine	79.97	47.70	47.530
4 equiv. of Oxygen	32.00	19.42	
	<hr/> 166.97	<hr/> 100.00	

This substance decomposes partially every time it is distilled with evolution of hydrobromic acid. It is rapidly acted on by ammonia.

Bromacetate of Amyl is obtained by heating hydrate of amyl with an excess of bromacetic acid, washing the product with water, and drying over chloride of calcium. It is an oily liquid, having a pleasant odour when cold, but if heated, acts upon the eyes and nose like the preceding. It boils at 207°C ., and decomposes partially every time it is distilled. Ammonia acts but slowly upon this substance in the cold.

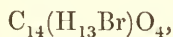
Two combustions of this substance gave the following results :

- I. gram.
 .5091 of Bromacetate of Amyl gave
 .7658 of Carbonic Acid and
 .2916 of Water.
- II.
 .4829 of Bromacetate of Amyl gave
 .7071 of Carbonic Acid, and
 .2675 of Water.

Percentage composition.

		I.	II.
Carbon	40·08	39·97
Hydrogen	6·41	6·15

which agrees with the formula



as may be seen by the following comparison of the theoretical and experimental numbers :

14 equiv. of Carbon	84·00	40·19	40·02
13 „ Hydrogen	13·00	6·22	6·28
1 „ Bromine	79·97	38·22	—
4 „ Oxygen	32·00	15·37	—
	<hr/>	<hr/>	<hr/>
	208·97	100·00	

A curious relationship exists between the boiling points of the acetates and the bromacetates of methyl, ethyl, and amyl. Although constant boiling points have not been obtained with the bromacetic ethers, yet if the highest point at which the largest proportion comes over be taken, it will be found that the bromacetates boil at a temperature from about 82° to 86° C., higher than the corresponding acetates. Thus—

	Boiling point.		Boiling point.	Diff.
Bromacetate of Methyl	144°	Acetate of Methyl	58°	86°
„ Ethyl	159°	„ Ethyl	74°	85°
„ Amyl	207°	„ Amyl	125°	82°

A similar difference also exists between the boiling points of bromacetic and acetic acids.

Boiling point of Bromacetic Acid	= 208°
„ „ Acetic Acid	= 120°

88 diff.

Could these substances be distilled without decomposition, and a constant boiling point obtained, it is very probable that the numbers would agree much more closely.

Bibromacetic Acid.

This acid is formed when a mixture of bromine and acetic acid is heated in presence of light; also in small quantities when bromacetic acid is heated. It is difficult to obtain in large quantities. We are at present endeavouring to find a process by means of which it may be produced with certainty in any quantity.

Bibromacetic acid is a liquid boiling at about 240° C.; it is decomposed partially every time it is distilled, evolving hydrobromic acid. It does not solidify at 15° C. It is possible that by the continued action of heat it might be transformed into *tribromacetic acid*. Its specific gravity is very great.

Bromacetic acid forms salts with most bases; they are in general uncrystallizable.

Bibromacetate of Barium is deliquescent, drying up to a gum-like sticky mass.

Bibromacetate of Lead is uncrystallizable, drying up to a highly refractive transparent substance, attracting moisture, and becoming opaque. It is very soluble in water.

Bibromacetate of Silver is obtained by adding nitrate of silver to a solution of bibromacetic acid, when it falls down as a crystalline precipitate. It is decomposed by ebullition with water into bromide of silver and a soluble acid.

Two silver and one bromine determinations gave the following numbers :

I.

·922 of Bibromacetate of Silver gave
·4196 of Chloride of Silver.

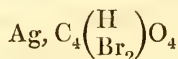
II.

·6446 of Bibromacetate of Silver, when heated with
carbonate of soda, &c., gave
·2154 of Metallic Silver,
·7160 of Bromide of Silver.

Percentage composition.

		I.	II.
Silver	33·0	33·41
Bromine	—	49·26

These numbers agree with the formula



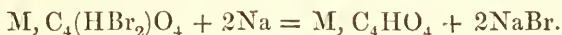
as may be seen by the following table :

	Theory.		Exp.
4 equiv. Carbon	24.00	7.364	—
2 „ Hydrogen	2.00	0.613	—
1 „ Silver	107.97	33.128	33.2
2 „ Bromine	159.94	49.074	49.26
4 „ Oxygen	32.00	9.821	—
	<hr/>	<hr/>	<hr/>
	325.91	100.000	

Bibromacetate of Ethyl is obtained by heating hydrate of ethyl with bibromacetic acid in a sealed tube, at a temperature of 100° C., washing the product with water, and drying over chloride of calcium.

It is a colourless liquid, heavier than water. It acts on the eyes and nose like the bromacetate of ethyl.

It is possible that if a salt of bibromacetic acid were treated with sodium or metallic zinc, an acid might be obtained standing to acetic acid, in the same relation as acrylic acid stands to propionic acid.



We have lately studied the action of ammonia on bromacetic acid, and have obtained some exceedingly interesting results. We find that when bromacetic acid is heated with ammonia, there is formed a large quantity of bromide of ammonium, and a beautiful white, sweet tasting substance which we think without hesitation we may say is *Glycocol*. We have made a combustion of this substance, gave the following numbers :

·3256 of Substance gave
·3837 of Carbonic Acid, and
·1920 of Water.

Percentage composition.

Carbon	3.21
Hydrogen	6.53

The formula

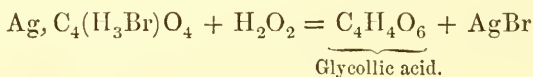
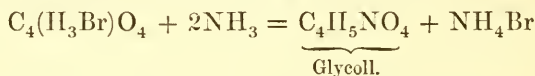
$$\text{C}_4\text{H}_5\text{NO}_4 \text{ requiring}$$

Carbon	32·0
Hydrogen	6·6

There cannot, therefore, be any doubt as to the composition of this product being identical to that of Glycol; nevertheless we hope soon to give some confirmatory numbers.

We also find that on boiling the bromacetate of silver in water, we obtain a powerful syrupy acid, and which has all the properties of glycollic acid.

The formation of glycol and glycollic acid from bromacetic acid may easily be understood by the following equations :



We hope when we have completed our investigations on the formation of glycol and glycollic acid, to give an account of the action of ammonia and of hydrate of silver on bromacetic acid, and also of the action of zinc-methyl and zinc-ethyl on these new bromo-acids.

V.—*On the Use of Gas as Fuel in Organic Analysis.*

BY A. W. HOFMANN.

SOME years ago* I described a gas-furnace which I then used for combustions. The apparatus in question furnished very valuable results, but has many imperfections which I did not leave unnoticed at that time. The wire-gauze over which the air-flame of the gas is lighted is rapidly destroyed and must be often renewed; frequently the wire-gauze becomes perforated during a combustion, the flame then descends, and the heat can no longer be regulated. The greatest inconvenience however of

* Journ. of the Chem. Soc., vol. vi, p. 209.

this furnace arises from the fact, that the temperature which it yields is barely sufficient for a combustion in the ordinary way; so that even substances which, when mixed with oxide of copper, readily burn in a charcoal fire, involve the necessity of completing their combustion by a current of oxygen. The simplicity of Liebig's original method, which has contributed so much to the rapid progress of organic chemistry, is thus more or less complicated.

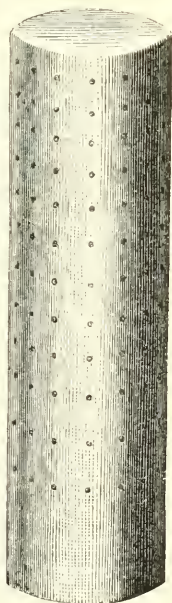
The combustion-furnace described by me has been repeatedly modified. The alterations, however, which have been suggested generally refer to special parts of the apparatus: the mode of admitting the gas has been changed: instead of the piston, which I had adopted, a system of valves or stop-cocks has been found by others more convenient, &c. In most cases, however, the original method of burning a mixture of gas and air over a wire-gauze has been retained. Since I was by no means satisfied with my apparatus, I have during the last two or three years tried nearly all the alterations which have been proposed by others, without, however, obtaining a furnace possessing all the qualities which I could have desired.

I therefore tried new constructions, and ultimately entirely gave up the old method. After much time and labour which I have devoted to this subject, I have at last arrived at an apparatus which has not only satisfied myself personally, but which has been rapidly adopted in many of the London laboratories.

In reply to several inquiries which have been addressed to me on this subject, I give in the following pages a short description of the new furnace.

Several years ago a peculiar clay burner was introduced, under the name of *atmopyre*, which I think has scarcely received from chemists the attention which it deserves. This burner is a hollow cylinder of burnt clay, closed at the top, open at the bottom, and with numerous perforations through the sides. Those which I use, and which are represented in fig. 1, are 3 inches high, of $\frac{7}{8}$ inch exterior, and $\frac{3}{8}$ inch interior diameter. The perforations are of about

FIG. 1.

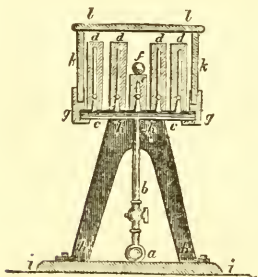


the thickness of a pin, are made in rows; their number varies, those which I employ have ten rows each of fifteen holes. From such a clay cylinder, loosely fixed upon an ordinary bat's-wing burner, the stop-cock of which has been appropriately adjusted, the gas burns with a perfectly blue flame which envelopes the cylinder and renders it in a short time incandescent.

These clay burners being readily obtainable and very indestructible, I have tried to construct a complete combustion-furnace for organic analysis, by appropriately grouping together a number of them. The result of the experiment has surpassed my most sanguine expectations.

The disposition of the apparatus being obvious from the accompanying wood-cuts, a few explanatory remarks may be sufficient.

FIG 2.



- a* Horizontal gas-pipe.
- b* Vertical gas-pipe, provided with stop-cock.
- cc* Bracket for burners.
- dddd* High clay burners.
- e* Low clay burner.
- f* Combustion-tube.
- gg* Wrought iron frame.
- hh* Cast iron supports.
- ii* Cast iron foot-plate.
- kk* Side plates of fire-clay.
- ll* Cover plates of fire-clay.

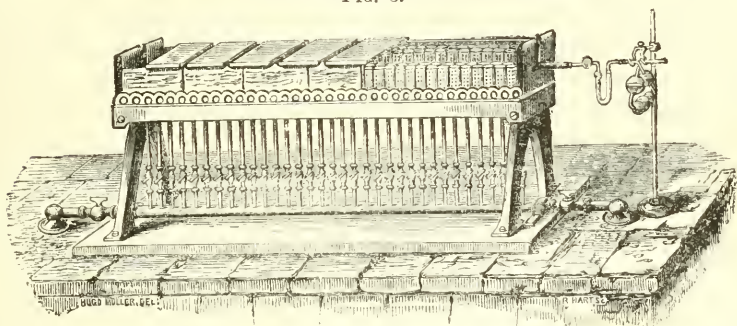
Into a brass tube, *a*, of from 3 feet to 3 feet 8 inches length and 1 inch diameter (shown in section in fig. 2), which communicates at both ends with the gas-main of the laboratory, there are screwed from twenty-four to thirty-four tubes, *b*. These tubes, $\frac{1}{2}$ inch thick and 7 inches high, are provided with stop-cocks, and carry brackets, *cc*, of $4\frac{1}{2}$ inches length and $\frac{5}{8}$ inch diameter, for the reception of five ordinary bat's-wing burners (each consuming from 3 to 4 cubic feet of gas per hour for a full luminous effect) upon which a corresponding number of clay-burners is fixed. These clay burners, *dddd*, have the dimensions before stated, with the exception of the middle one, which is only $1\frac{7}{8}$ inches high, and has only seventy or eighty

perforations. It serves as support for the combustion-tube, *f*, which is thus bedded in a channel of heated fire-clay. The system of brackets lying side by side acquires sufficient stability by a strong iron frame, *gg*, which rests upon two firm supports, *hh*, of cast iron, fastened down by screws upon the foot-plate, *ii*, likewise of cast iron. The iron frame, *gg*, has moreover a groove for the reception of moveable side plates of fire-clay, *kk*. They are of the same height as the high burners, over which they project, but about $\frac{5}{8}$ inch, in consequence of their resting

upon the frame *g*; lastly, *ll* are covering plates, likewise of fire-clay, which are supported by the side plates, *kk*.

The whole disposition of this apparatus will be best understood by a glance at the perspective view given in fig. 3.*

FIG. 3.



In the front part, contiguous to the potash-apparatus, the side plates and the covering plates are omitted, in order to show the disposition of the burners. During the combustion, however, all the burners are inclosed, as exhibited in the posterior part of the apparatus.

It deserves to be noticed that the efficiency of the furnace essentially depends upon the correct disposition of the gas-jets. The most appropriate space between the several burners, according to numerous experiments made for the purpose, is about $\frac{1}{8}$ inch. It is very important, for the attainment of a perfectly uniform temperature, that the several brackets bearing the burners should be equidistant. Their position is therefore specially secured by every bracket being fixed in an aperture formed in the iron frame, *gg* (fig. 2).

The use of the furnace scarcely requires any special remark. According to the length of the combustion-tube, from 8 to 10 stop-cocks (under all circumstances the largest possible number), are opened at once at the commencement of a combustion. If care has been taken to regulate the amount of gas, either by the stop-cocks in the horizontal gas-pipe, or by those in the separate supply-tubes, the lighted portion of the furnace, in 10 or 12 minutes, will be in a state of perfect incandescence, comparable only to the ignited mass of charcoal in an ordinary combustion-furnace.

* The engraving is taken from the 7th edition of Fownes' Manual of Chemistry, London, 1858. John Churchill.

After this it is only necessary to open the remainder of the stop-cocks in appropriate succession, to insure a slow and regularly progressing combustion. The time required for the completion of an analysis varies from 40 minutes to an hour. Only in extraordinary cases a longer time may be required.

The heat obtained by this furnace is extremely uniform, and since it is conveyed to the combustion-tube chiefly by radiation from the incandescent mass of surrounding clay, every part of the tube is equally heated. It is in this respect especially that the new apparatus differs from all former contrivances of this kind. The temperature which it is capable of yielding is entirely at the command of the operator. When strained to its full power, it gives a heat equal to that of the strongest charcoal combustion-furnace, at which even the most refractory Bohemian tubes readily fuse; by appropriately adjusting the stop-cocks, however, it is possible to maintain the furnace at any desired temperature, especially since it is only necessary to look into the channel, when, with a little practice, a correct idea of the temperature is rapidly obtained from the colour of the glowing cylinders. It deserves, however, to be noticed, that the apparatus furnishes rather more than less heat than is generally required; it is preferable, therefore, under all circumstances, to protect the combustion-tube by a metallic shield: for this purpose ordinary brass-wire gauze* may be conveniently employed; which is more easily manipulated, and may be used longer than the thin copper or brass plate generally employed.

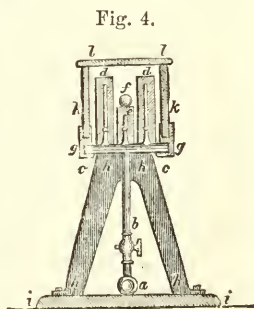
From what has been stated it is obvious that the furnace may be used in many operations in which charcoal has hitherto been considered almost indispensable. During the time I have had it in use, it has served in all kinds of analyses, from the combustion of ether to the carbon-determination in cast iron. It is scarcely requisite to be mentioned, that the combustion may be made with or without oxygen, as the case may necessitate. In all other tube-operations, in passing gases or vapours through red-hot tubes (preparation of propylene gas), in reducing copper-turnings, &c., the apparatus may be used with equal advantage; for the latter operation, which has to be so frequently repeated, it is found convenient to re-arrange the burners in such a manner as to obtain, by the introduction of a second row of small burners in the place of large burners, two gutters or channels, in which two glass tubes, connected by means of caoutchouc with the same hydrogen-apparatus, may be heated at once. In like manner two combustion-tubes, similarly filled with

a similar mixture, have been actually heated simultaneously. If short combustion-tubes are to be heated, such as are used in nitrogen-determinations, an additional advantage may be obtained by simultaneously operating on both sides of the apparatus.

One of the great advantages of this furnace is its durability; one that I have had in almost daily use during ten months, is as good as new at the present moment. The clay burners, as I have stated already, are very indestructible, but even in case of a burner splitting, it may be rapidly removed and replaced, even during an analysis. The clay plates also, when well burnt, are very durable, and often serve for months, even after they are split. At first, I was somewhat afraid the minute holes in the clay burners might become stopped up by carbon; but the mixture of gas and atmospheric air is so perfect, and the diffusion of the combustion is so great (in the apparatus which I use, the gas issuing from between 24,000 and 25,000 apertures), that neither upon the burners nor in the perforations is the slightest trace of carbon deposited.

It remains now only to mention a few experiments which were made, in order to determine the quantity of gas consumed by the apparatus. These experiments were performed in the laboratory of my friend, Mr. J. J. Evans, of the Chartered Gas Company, who kindly placed his instruments at my disposal. It was found that a combustion, lasting one hour, and requiring the whole length of the furnace (34 rows of burners), consumes from 80 to 90 cubic feet; the maximum ever observed being 100 cubic feet. For a carbon-determination, with 24 rows of burners, which generally lasts about 40 minutes, from 50 to 60 cubic feet are required; for a nitrogen-determination, from 25 to 30 cubic feet. Perfectly similar results have been observed by Dr. Watson. From these data it is obvious that this apparatus is a very economical one, especially in localities where gas is cheap and charcoal dear. In laboratories, therefore, where many combustions are made, the saving of fuel will readily cover the original outlay for the furnace.

The cost of the apparatus and the consumption of gas can be still further diminished by reducing the number of the rows of burners from 5 to 3. Fig. 4 shows the section of such a furnace, which has furnished me good results.



Such a furnace of course does not yield the same degree of temperature as the larger one, it also requires a few minutes more to produce the full effect; but in few cases will a higher temperature be necessary for combustions. Such a smaller apparatus is also very useful in lectures, when a further simplification may be effected by a diminution of the number of the stop-cocks.

In conclusion, I offer my best thanks to my friends Dr. Watson and Dr. H. Müller, whose interest in the apparatus has greatly facilitated its construction. My thanks are also due to Mr. R. H. Hess, who was entrusted with the manufacture of the furnace, and to whose perseverance, during many alterations, I am indebted for an apparatus which I should not like to miss any more in my researches.

VI.—*On the Chemical Action of Water on Soluble Salts.*

BY DR. J. H. GLADSTONE, F.R.S.

IN pursuing my researches on chemical affinity among substances in solution, it seemed desirable to ascertain, if possible, what specific chemical action water exerted on a salt. Unfortunately my experiments in this direction have not led to any such conclusive result as I had hoped; yet, during the course of the inquiry, many observations were made which I believe to be new, and some of which I think are not unworthy the notice of chemists.

In order to bring these observations clearly before the minds of others, it may be well to associate them with the leading trains of thought that presented themselves to my own mind during the investigation; and, as in a difficult discussion it is very necessary to examine the simpler before attempting the more complex phenomena, it will be wise to confine the attention first to simple salts, and indeed to begin by trying to ascertain what is the action of water on such a salt *before* it dissolves it.

Anhydrous salts will frequently absorb water, and still remain solid bodies, either amorphous or crystallized. In such a case, the water combined in the solid form is always in atomic relation with the salt itself. The language of chemists implies the general belief

that a certain number of equivalents of water are then simply added to the original salt; yet great heat is often evolved, and a change of colour frequently ensues.* I know of no reason to think that the water in such a case has been decomposed by the salt (whose composition may be expressed by the general formula MR), and that the resulting solid contains any such compound as MO,HR , though should any one choose to advance such a view he would not be wholly without arguments to support it.

These "hydrated" salts are usually, but not always, soluble in water. When solution does take place, those difficulties, as to their rational composition, of which we have already seen the commencement, increase; for there is now scope for more varied chemical actions, and consequently for a wider range of speculation. The water may act merely as a solvent; or it may unite without decomposition with the dissolved salt, becoming an integral part of it; or it may exert an action similar to what usually takes place when two binary compounds are united under such circumstances that all the resulting bodies are free to act and react, namely, that reciprocal decomposition ensues, each electro-positive element combining with each electro-negative one in certain proportions; or the ultimate result may be due to two or more of these modes of action in conjunction.

Usually when a "hydrated" salt is dissolved in a minimum of water, nothing is observable beyond a change in its state of aggregation, and the new physical properties, and the absorption of heat resulting from that. No change of colour, as far as I can find, ever ensues. A change in fluorescence may occur.† There is no atomic relation between the quantity of salt dissolved, and the quantity of water, indeed the ratio varies with the degree of temperature. Here we *seem* to have the simplest case of solution, such as we necessarily conceive when a salt dissolves in ether, or a fat in an essential oil.

When an anhydrous salt, which will not combine with water to produce a solid compound, dissolves in that liquid, the same phenomena usually present themselves, except that a change in colour

* For a case in point, and some remarks on it, see my paper "On the Colour of Chloride of Copper in Different States of Hydration." *Quart. Journ. Chem. Soc.*, viii, 211.

† As in the case of crystallized salts of uranium, which are much more fluorescent than their saturated solutions. See the paper of Prof. Stokes, *Phil. Trans.*, 1852, 517. This observation, as every other quoted or reasoned on in this communication, has been verified by myself.

may occur; as in the case of red prussiate of potash, which gives a green saturated solution.

Sometimes, however, an evident decomposition ensues, the hydrogen and oxygen of the water combining each with one of the elements of the other binary compound, and the products of this action remaining uncombined. This is common among the compounds of the non-metallic bodies—as, for instance, the chlorides of phosphorus,—and is not unknown among what are more properly called salts, for instance chloride or nitrate of bismuth, or sulphate phosphate or citrate of ammonia. In such cases the decomposition makes itself manifest by the separation of the one resulting substance from the other. The bismuth salt treated with water forms an insoluble subsalt; the compound of ammonia with a polybasic acid gives off some of the volatile alkali when its solution is heated, while the liquid itself becomes acid. It is certain, however, that in the vast majority of cases of solutions of salts, no such interchange takes place, with the production of a new oxygen and a new hydrogen compound uncombined; if chloride of copper be dissolved, no oxide of copper, or subsalt, is precipitated, and no hydrochloric acid can be boiled off. Yet it has been contended that a haloid salt in dissolving ceases to be of the constitution MR , and becomes MO, HR ; only that the two new products, instead of separating, form one compound body. When this theory was started, there was supposed to be a wide difference in the essential constitution of haloid and other salts; our views have now changed, and there seems to me now no logical grounds on which, if we consider a haloid salt in solution to be MO, HR , we can stop short and refuse to consider this as the general expression of any salt in solution.

I was unacquainted with any argument of weight in support of this hypothesis; yet, on the other hand, it had never been actually disproved. Analogy, too, led me to view it with some favour, for it seemed reasonable to suppose that water might act like hydrochloric acid, or a similar hydrogen compound, and that possibly an aqueous solution of a salt might resemble a solution of ferric phosphate in hydrochloric acid, which contains portions of both the original salt and the hydracid, mixed with ferric chloride and phosphoric acid.* The action of HO on MR would by analogy

* See my paper, in the *Quart. Journ. Chem. Soc.*, ix, 152. Of course water was present in the reaction alluded to there, but I have repeated it in absolute alcohol with a similar result.

result in a reciprocal decomposition, MO and HR being formed—either separate or in combination—while portions of the original HO and MR coexisted in the same solution.

But how was this to be decided? By all analogy it might be anticipated that by increasing the amount of HO more MR would be decomposed, just as the addition of more hydrochloric acid to a solution of ferric phosphate in that acid, produces more ferric chloride and heightens the colour. The action of water when added to a saturated solution of a salt becomes therefore a matter of peculiar interest.

That such an addition of water produces a decomposition is sometimes evident from the separation of a precipitate—and that in several different ways. Thus:—

Pentachloride of antimony, as is well known, though soluble in a small amount of water, is decomposed by a larger quantity, giving rise to hydrochloric acid, and an oxychloride of the composition SbClO_2 , according to Peligot.

A strong solution of ferric sulphate, if diluted with water, deposits a subsalt, $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 + 7\text{HO}$.*

The intensely blue solution of crystallized ammoniacal nitrate or sulphate of copper in a little water is perfectly clear, but on dilution it becomes turbid from the separation of a subsalt, the quadrobasic sulphate, while free ammonia is perceived in the solution.

Nitrate of bismuth, if slightly acid, dissolves in a little water, but forms a white precipitate, of varying composition, when this is poured into a larger quantity.

In all these cases, the amount of precipitate increases, within certain limits, with the amount of water added. The full action of the water also does not take place instantly. Yet it must be borne in mind that not one of these salts is of simple constitution after the type MR, and that the products of decomposition are never MO, but some new salt of complicated composition. There is this difference too between these cases and all those instances of reciprocal decomposition which are recorded in my paper “On the circumstances modifying the action of Chemical Affinity,” that here a large amount of water, many equivalents in fact, is required before any trace of the insoluble compound is formed.

* According to Scheerer, this is $2(3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3) + 9\text{HO}$, but the specimens analyzed by me contained more water.

That the addition of water to a saturated aqueous solution of a salt produces some chemical change is sometimes apparent from a change in colour. This phenomenon was closely examined.

It might be anticipated, *a priori*, that a certain amount of salt would have the same absorbent effect on a given number of rays of light, whether it were dissolved in much or in little water, and that, as the absorbent power of water is practically *nil*, it would appear to the eye of precisely the same depth and character of colour in the two cases. And this actually happens in the majority of instances; but, to perform the experiment, it was, of course, necessary to make the same quantity of light impinge upon the solution before and after dilution, and this required a special contrivance. Colourless cylindrical glasses of uniform diameter and of the same size were procured, and they were each closed at one end with a flat plate of glass. These were placed side by side in a wooden frame (something like that of an ordinary stereoscope), which was painted black within, and so made that it prevented any light from passing into the cylindrical glasses except by the two ends. This frame was supported in such a manner that the glasses were vertical, with a space of a foot or thereabouts intervening between them and a sheet of white card-board placed beneath. The glasses so situated were of course capable of holding solutions, and it is evident that the light transmitted through them to the eye of an observer standing above must come through the flat ends of the cylinders, which were of uniform size, and equally illuminated from the white sheet below. It is evident, too, that any alteration in the bulk of the liquid will not affect the quantity of light that enters by the end of the cylinder; and that the fact of all experiments being comparative will eliminate all errors that might have arisen from the difference of light at different hours, or any similar cause. As this little apparatus will be frequently referred to, I will give it a name, and since its principal use is in judging by the eye of the quantity of colour in two solutions, it may be appropriately designated the *Isoscope*.

For the purpose of determining whether the addition of water to a saturated solution of a salt causes it to absorb more or less light, the solution to be examined was divided equally between the two cylindrical glasses, so that when they were looked through from above they appeared identical in colour; water was then added to one of them, and if any change was effected by it, it became at once visible by comparison with the other. It was found neces-

sary to avoid focusing the eye at any particular part of a solution, when diluted so as to be very deep, but a little practice will soon enable the observer to avoid this, especially when the solutions are looked at from some considerable distance (five or six feet) above them. It is desirable also to place the head in such a position that the line joining the two eyes shall be at right angles to the line joining the two glasses, for if each eye be immediately over one of the glasses, a slight fallacy results, apparently from the unequal strength of the two eyes. The accuracy with which slight differences in intensity of colour may be observed, varies with the nature of the colour, the degree of illumination, and doubtless the sensitiveness of the observer's eye. In my case I can generally detect, under ordinary circumstances, a variation of 1 in 50. Differences in the *character* of the colour are, of course, easily recognized.

In this manner, the saturated solutions of many simple salts were examined, and where the saturated solution was too intensely coloured to be practically available, a slightly diluted solution was placed in each glass, and with one of them additional water was mixed. The following salts appeared to be unaffected by water, as to their power of absorbing the rays of light:—

Ferrous sulphate.	Terchloride of gold.
Ferric nitrate.	Terbromide of gold.
Ferric meconate.	Protochloride of platinum (in
Ferric comenate.	hydrochloric acid).
Ferric comenamate.	Bichloride of platinum.
Ferric gallate.	Bichloride of palladium.
Nitrate of nickel.	Chromate of potash.
Nitrate of cobalt.	Ferrocyanide of potassium.
Sulphate of copper.	Ferridecyanide of potassium.
Chloride of chromium.	Nitroprusside of sodium.
Acetate of chromium.	Sulphindigotic acid.
Chromate of chromium.	Sulphindigotate of ammonia.
Nitrate of uranium.	Carbazotate of copper.
Chloride of uranium.	Pentasulphide of potassium.
Sulphate of ceric oxide.	

Some dissolved salts were found to vary in the intensity of their colour, but not in the character of it, on dilution, thus:—

Ferric acetate became considerably darker.

Ferric tartrate became slightly paler.

Chromic sulphate (green modification) became paler.

Many dissolved salts were found to vary in the character of their colour, according to the state of dilution, thus:—

Ferric chloride becomes more yellow, that is to say, passes from a red orange to an orange yellow.

Ferric citrate becomes paler and more yellow.

Ferric sulphocyanide changes from an intense and pure red to orange, and on further dilution to yellow; but when this colour makes its appearance a decomposition manifests itself by the formation of a yellow precipitate.*

Chloride of nickel passes from a yellow to a blue green.

Iodide of nickel suffers a similar change, though when strong it does not transmit so much light as the chloride does.

Chloride of cobalt becomes paler and of a more decided pink.

Iodide of cobalt passes from a deep green to pink.

Acetate of cobalt becomes slightly paler, and assumes somewhat of a yellower tint.

Sulphocyanide of cobalt passes from a magnificent purple blue through every shade of purple till it becomes of the ordinary red or pink colour of cobalt salts in solution.

Chloride of copper passes from green to blue.

Bromide of copper suffers a similar change.

Acetate of copper becomes much paler, and passes from a greenish to a more pure blue.

Permanganate of potash becomes paler and of a redder purple.

Chromic acid passes from red to an orange brown, then to a purer orange, which becomes paler on further dilution.

That these changes of colour are due to the action of the water, and not to any merely physical cause, is proved by the fact that dilution with alcohol does not occasion them. Chloride of copper, for instance, dissolves in absolute alcohol of a bright green colour, and chloride or sulphocyanide of cobalt of a magnificent bluish purple, but when examined by the isoscope, these solutions are found to be unaffected by the additions of more absolute alcohol, either in respect to the intensity or the character of their colour. If water be added to the alcoholic solution, the change of colour ensues more or less perfectly according to the relative amount of the two liquids; and if alcohol be added to a somewhat dilute

* This decomposition has been investigated by Dr. Claus; see *Annal. Chem. u. Pharm.* July, 1856. He seems to be unaware that the sulphocyanide may be diluted till it appears of a yellowish orange, without any precipitate forming, even after many days.

aqueous solution of these salts, the primary colour is more or less restored. Ferric sulphocyanide, however, seems to form an exception. A very large quantity of absolute alcohol produces the same change in the colour of this substance that a much smaller quantity of water does, and on long standing, a little yellow substance separates. I do not believe that this depends on any water in the alcohol itself; for that employed by me was of specific gravity 790, and it is hard to conceive that any trace of water should leave the strongest alcohol to act upon a salt, and effect a change which usually requires its presence in overpowering quantity.

A glance at the list of salts which change colour on the addition of water will suffice to show that they consist of little else than acetates, and a peculiar group of "haloid" salts, namely, compounds of chlorine, bromine, iodine, and sulphocyanogen, with iron, and the allied metals, nickel, cobalt, and copper.

These changes of colour, though consistent with the idea of the water added to a saturated solution decomposing more of the original salt MR , and thus forming more MO, HR , are very far from proving that hypothesis. They may be attributed to the formation of a higher hydrate; and other hypotheses might easily be invented. It seemed, however, a matter of interest to try whether the change of colour produced by water in a solution of such a salt as acetate of copper was analogous to the change that takes place on the addition of another hydrogen compound, for instance, hydrochloric or sulphuric acid*. Now, in both cases, a reduction of the colour ensues; and in the case of the acid, it takes place in a diminishing ratio, that is, each addition of acid has a smaller effect (as compared with its quantity) than the preceding. Does the action of water exhibit a similar ratio?

Experiments were performed to determine this. A portion of a saturated solution of acetate of copper was divided equally between the two vertical glasses of the isoscope. The one was kept as a standard; to the other a known amount of the same saturated solution was added, and as that of course increased the colour, water was added till it was brought down again to that of the standard. The ratio between the amount of water added and the amount of coloured salt which it could render invisible, so to speak, gave what was required. Two experiments were made with the same solution.

* Phil. Trans. 1855, pp. 222, 223.

Orig. amount of Acetate of Copper Solution.	Amount of Acetate of Cop- per solution added.	Water required.		Reducing effect of each addition of Water.	
		Exp. I.	Exp. II.	Exp. I.	Exp. II.
Pts.	Pts.	Pts.	Pts.	Per cent.	Per cent.
100	8	60	..	13·3	
100	16	116	..	14·3	
100	24	180	..	12·5	
100	32	244	..	12·5	
100	40	..	330	..	12·1
100	48	352	405	14·8	10·7
100	56	..	535	..	6·1
100	64	596	615	6·5	10·
100	72	..	790	..	4·6
100	80	980	975	4·2	4·3
100	88	..	1180	..	3·9
100	96	1500	1440	3·1	3·1

Both these experiments indicate that the effect of additional quantities of water is in a decreasing ratio, at least, after the addition of four or five times its bulk of water to the saturated solution, about which point the two experiments show a certain irregularity and discrepaney. About this point, also, the change to a somewhat purer blue takes place.

On mixing water with a solution of ferric acetate, the colour is considerably deepened, but on standing awhile, the solution becomes nearly as pale as originally.

The following series of observations was obtained with ferric sulphocyanide :—

Orig. amount of Ferric Sulphocyanide Solution.	Amount of Sulphocyanide Solution added.	Water required.	Reducing effect of each addition of Water.
Pts.	Pts.	Pts.	Per 100 pts.
100	10	24	4·2
100	20	44	5·0
100	40	80	5·5
100	60	128	4·2
100	80	204	2·6
100	100	296	2·2
100	120	384	2·3
100	140	468	2·4
100	160	556	2·3
100	190	692	2·2

Within the range of these observations, which, as may be supposed, did not commence with a saturated solution, and which terminated long before the salt became yellow, there is evidently more than one change of ratio in the reducing effect of successive additions of water. The ratio at first increases, then rapidly decreases, and attains a kind of uniformity, which, however, seems to show another but very slight rise and fall.

The irregularity of these results rather militates against the idea of water acting on salts in the same way as a hydracid.

A still stronger argument against this hypothesis was found on a comparison of the rays absorbed by dilute and strong solutions of those salts that vary in the character of their colour according to the amount of water. It invariably happens that the dilute solutions, while they transmit every ray that was transmitted by a strong solution of the same salt, transmit also some that were absorbed by it. To take a particular instance, blue sulphocyanide of cobalt absorbs at once those rays of the prismatic spectrum which lie about the fixed line D; the red sulphocyanide transmits them perfectly: hence it may be concluded that after a certain dilution no more blue sulphocyanide is left, a conclusion at variance with the supposition that HO acting on CoCsy (blue salt) produces CoO,HCsy (red salt) + H₂O + CoCsy, the amount of the last substance diminishing as the water increases, but never entirely disappearing. The nature of the absorption indicates rather that the strong solution contains the compounds present in the dilute solution *plus* some other; and a close prismatic examination of the 'haloid' salts that change colour has furnished me with a remarkable confirmation of this view. It is founded on the fact deduced by *a priori* reasoning in my paper on the use of the prism,* and demonstrated in a more recent paper,† that "when two bodies combine, each of which exerts a different influence on the rays of the spectrum, the one constituent will absorb certain rays, and the other certain other rays, and the dissolved salt itself will transmit only those rays which are not absorbed by either, or in other words, only those which are transmitted by both." Now strong solutions of ferric chloride, chloride and bromide of copper, chloride and iodide of nickel and of cobalt, exhibit not only the absorption due to the respective metals, but another absorption which can be identified with that produced by the halogens themselves when simply dissolved in water; while, when these solutions are diluted, they cease to produce this second absorption, and give precisely the same prismatic image as any compound of the same base with a colourless acid. This is explained in detail with figures in the paper already referred to.† It is certainly a suggestive fact, and shows, I think, most clearly, that there is some difference of arrangement among the elements of the dissolved salt and the water, according to their proportional

* Quart. Journ. Chem. Soc. April, 1857.

† Phil. Mag. Dec. 1857.

amount, and the degree of temperature; but what is that difference? The peculiar absorbent power exerted by bromine shows itself in the green solution of bromide of copper, but there is certainly no free bromine present, and it will hardly avail us to suppose that such a solution contains the true CuBr , and that the change of colour on dilution arises from the formation of a compound of oxide of copper with the colourless hydrobromic acid; for there would still remain the question—why should bromine affect the light when in combination with copper, while it does not do so when combined with hydrogen, or potassium, or indeed any other metal beyond this particular group and the congeners of gold? Besides anhydrous bromide of copper, which certainly has the greatest claim to be considered CuBr , is not green but black.

DOUBLE SALTS.

The action of water on double salts is a still more complicated problem, for beside all the questions that arise in respect to simple salts, there is the additional inquiry—whether water separates the two constituents of which the double salt is composed. This latter question, however, is more capable of decision than some previously discussed.

That a double salt is not always resolved into the two simple salts which we suppose constitute it, requires no elaborate proof. The iodide of platinum and potassium dissolves easily in water, though the iodide of platinum itself is insoluble; while, on the other hand, the potassio-chloride is sparingly soluble, though each of the chlorides supposed to be contained in it dissolves readily in water.

It is very conceivable, however, that in some cases a partial decomposition may take place; indeed some of Professor Graham's experiments seem to indicate this. He states,* that when alum, or bisulphate of potash, is diffused, one of the constituents passes out of the cell in greater quantity than the other. Now if these double salts are partially decomposed by the water, this is precisely what might be anticipated; and there is nothing else than water present to decompose them.

Should water exert such an action, it might be expected that the action would be increased by the addition of more water.

* Phil. Trans., 1850, p. 19.

There are cases in which water, when added in above a certain amount, does decompose a double salt. Thus colourless crystals of the iodide of mercury and potassium will dissolve in a little water, but the addition of a larger quantity causes the separation of the insoluble yellow iodide of mercury; and water added to a saturated aqueous solution of sulphocyanide of silver and potassium gives a curdy precipitate of sulphocyanide of silver.* In each case the more water is added the more complete the decomposition.

As double salts in a crystallized condition sometimes differ considerably in colour or shade from the simple salt of that base to which the colour is due, it was thought that if an increasing decomposition by water took place, it would make itself visible by a change of colour or shade when a strong solution was diluted in the isoscope. It was found, however, that the solution of a double salt containing a coloured constituent, has, generally speaking, precisely the colour and shade of that constituent; thus 200 grms., or one equivalent, of crystallized sulphate of copper and ammonia, gives precisely the same chromatic appearance when dissolved in water as 125 grms., or one equivalent, of crystallized sulphate of copper. Thus it was impossible to derive any information from the fact, that a solution of that salt, or the corresponding potash salt, or potash chrome alum, or the sulphate of nickel and potash, did not change in colour when diluted. The double chloride of platinum and potassium, the double iodide of the same, the analogous gold salt, and the hydrochlorate of chloride of gold, are also unaffected in colour by the further addition of water. What is more to the point is this—that the red bichromate of potash does not pale in colour on dilution, or become more yellow, as would be the case were more of the free acid and the neutral potash salt formed; and the bicomensamate of iron, which is red, remains unchanged, although the neutral salt is purple, and the comensamic acid itself colourless.

On the other hand, instances are not wanting of double salts, the solutions of which change colour on dilution. Thus, the compounds of chloride of copper with chloride of sodium, chloride of ammonium, chloride of platinum, or hydrochloric acid, though green when dissolved in the minimum of water, become blue on dilution, just as chloride of copper itself does; but they require a larger amount of water to produce the change than is requisite in the case of the simple salt. Red potassio-chromic oxalate varies

* Described by Gössman, *Ann. Pharm.* Oct. 1856.

in intensity of colour by dilution, becoming sometimes paler, and at other times darker. The strong solution of white iron alum becomes redder on dilution, and Rose* has shown this to be due to the formation of a slightly soluble basic salt.

If a double salt be resolved on solution more or less into its simple salts, each of these will assuredly obey the law of reciprocal decomposition with any other salt that may be present. That this reciprocal action does take place between an ordinary and a double salt is beyond question; but that the elements of the latter have separated to produce it, is not so easily ascertained. One form of the experiment, however, occurred to me that seemed to be of a somewhat crucial character. Acetate of copper is of a much deeper blue than an equivalent amount of the sulphate, and this last, as stated above, is identical in colour with the double potash salt. If on mixing the sulphate of copper and potash with the acetate, the double salt should preserve its integrity, it is not very easy to conceive of a reciprocal decomposition, for the acetate itself is strictly monobasic, but if the double salt should separate to any extent, the free sulphate of potash will certainly suffer reciprocal decomposition with the acetate of copper, and as a portion of the copper will then be combined with sulphuric acid, a reduction of the colour will ensue. Accordingly, two equal portions of acetate of copper solution were mixed in the isoscope, the first with an equivalent of sulphate of copper, the second with an equivalent of double sulphate of copper and potash. The second mixture appeared somewhat lighter in shade than the first, and on the addition of three equivalents to each, the second became of a distinctly purer and paler blue. A similar experiment was made with the intensely scarlet bromide, and the pale yellow hydrochlorate of the chloride of gold. The addition of the latter compound reduced the colour of the bromide, though of course the mixture contained a larger amount of gold than the scarlet solution. It may be objected to this reaction that there probably exists a hydrobromate of the bromide of gold analogous to the chlorine compound; but that will not account for the reduction of colour, since the addition of hydrobromic acid to the neutral bromide does not render the solution paler.

In respect, then, to double salts it may be concluded that some are resolved by water more or less into two distinct salts, while

* Pogg. Ann. lxxxiii, 132.

others preserve their integrity in solution; but what determines this difference does not yet appear.

In respect to the general question of the chemical action of water on a soluble salt, I feel that no satisfactory conclusion has yet been arrived at; the idea that a reciprocal decomposition takes place between the two compounds has received no confirmation from my inquiry, unless in exceptional cases. The results rather militate in my opinion against that supposition, and tend to convince me more and more that the actual state of a dissolved salt is beyond the expression of any of our formulæ.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

January 21st, 1858.

Dr. LYON PLAYFAIR, C.B., President, in the Chair.

The following Gentlemen were elected Fellows of the Society:—

Arthur Nield, Esq., Bowdon, near Manchester.

Richard Rumney, Esq., Ardwick Chemical Works, Manchester.

Daniel Hanbury, Esq., Plough-court, Lombard-street.

Dr. Daubeny read and commented upon a communication he had received from Baron Liebig, relating to some experiments he had made on the absorptive power of soils, in continuation of Professor Way's experiments.

Dr. Daubeny also brought under the consideration of the Society, the experiments of Wöhler and Deville on the direct formation of nitride of titanium by the ignition of metallic titanium in air or nitrogen, and suggested that the source of volcanic ammonia might be a nitride of a similar description, that of boron for instance, which by the action of steam would be resolved into boracic acid and ammonia.

Dr. Hofmann exhibited and described an improved form of gas-combustion furnace which he had recently had constructed; in this furnace, the gas is burnt from numerous small openings in clay cylinders, which thereby become red hot, so that, as in the original charcoal furnace, the combustion tube is surrounded by ignited solid, and the supply of oxygen or air from gasometers is rendered unnecessary.

Dr. Frankland also exhibited a combustion furnace which had been arranged by Professor Von Babo. In this furnace the gas

was burnt in a series of modified Bunsen's burners; the combustion tube was surrounded by ignited solid, and the stopcocks were replaced by keys resembling those of a musical instrument.

A paper was read:—

“On the chemical action of Water on soluble Salts;” by Dr. Gladstone.

February 4, 1858.

Dr. LYON PLAYFAIR, C.B., President, in the Chair.

The following donations were announced:—

“The Journal of the Geological Society:” from the Society.

“Proceedings of the Liverpool Literary and Scientific Society:” from the Society.

“The Pharmaceutical Journal:” from the Editor.

“The Journal of the Society of Arts:” from the Society.

The following were elected Fellows of the Society:—

F. A. Manning, Esq., 54, Archer-street, Paddington.

P. J. Worsley, Esq., 4, Taviton-street, Gordon-square.

W. F. Squire, Ph.D., 277, Oxford-street.

J. F. Watson, M.A., M.D., 54, Archer-street, Kensington-park, W.

Dr. Hofmann, described some experiments in which he had been recently engaged upon poly-atomic ammonias.

February 18, 1858.

Dr. LYON PLAYFAIR, C.B., President, in the Chair.

The following were elected Fellows of the Society:—

T. H. Henry, Esq., 44, Lincoln's-inn-fields.

J. Augustus Matthiessen, Ph.D., 1, Torrington-street.

A paper was read:—

“On the Iodo-sulphates of the Cinchona Alkaloids;” by Dr. W. Bird Herapath.

March 4, 1858.

Dr. LYON PLAYFAIR, C.B., President, in the Chair.

The following were elected Fellows of the Society:—

Sir Robert Kane, F.R.S., Dublin.

J. T. Hobson, Esq., Ph.D., 34, Cleveland-square, Hyde-park.

W. Thornwaite, Esq., 123, Regent-street.

The meeting was then adjourned to enable the Members to attend the Bakerian Lecture at the Royal Society.

March 18, 1858.

Dr. LYON PLAYFAIR, C.B., President, in the Chair.

The following donations were announced:—

“Catalogue of the Antiquities in the Museum of the Royal Irish Academy.”

“Recherches sur la diffusion du Fluor : par M. J. Nickles.”

“Transactions of the Royal Scottish Society of Arts.”

“Kritische Zeitschrift fur Chemie, Physik, und Mathematik.”

The following were elected Fellows of the Society:—

John Purdue Bidlake, B.A., 9, Upper Barnsbury-street, Islington.

Edward Dalziel, M.D., F.R.S.E., Edinburgh.

Alexander Goaler, B.A., The College, Hurstpierpoint, Sussex.

Thomas Hyde Hills, Esq., 338, Oxford-street.

Henry Wollaston Hutton, B.A., Spordlington, Market Raisin, Lincolnshire.

David Oldfield, Esq., Boscombe Lodge, Finchley-road.

The following papers were read:—

“On the action of Bromine on Acetic Acid:” by Messrs. Perkin and Duppa.

“On a Poison obtained from Arrows:” by Mr. Henry Hancock.

NOTICES
OF
PAPERS CONTAINED IN OTHER JOURNALS.

*Extract of a Letter from Baron Liebig to Dr. Daubeny, dated
December 25, 1857.**

“I HAVE published a series of experiments on some properties of soils, by which I think I have completed the researches instituted by Professor Way, respecting their capacity for absorbing the soluble constituents of manures.

“My experiments were limited, to those constituents which are presented to plants from natural sources, and to the conditions necessary for rendering them soluble and absorbable by the roots.

“I was a little astonished to find, that the cause of this solubility did not appear to be traceable to circumstances attributable to the plant itself, but that something inherent in its own organization must co-operate with the actual conditions in which it was placed, in order to enable it to extract its food from the ground.

“The potassa belonging to silicate of potassa is absorbed by all kinds of soil, but not so the silicic acid accompanying it. If a solution of silicate of potassa be brought into contact with soils rich in organic matters, the potassa is absorbed, but the silica remains in the solution.

“From a solution of phosphate of lime, or of phosphate of magnesia, in water saturated with carbonic acid, soils absorb the phosphoric acid, whilst they allow the lime still to remain in the solution.

“Thus the inference deducible from my experiments is, that land plants do not receive their food from a solution of the ingredients already present in the soil, but that they abstract or absorb it directly from the soil itself, through the joint agency of water and of a force inherent in their roots.

“Sometimes we find stones in meadows covered over with striæ, exhibiting a kind of network, which is produced by the corrosive action of the roots of plants in contact with them.

“It has hitherto been assumed that a plant possessed a decomposing power as well as a secreting one. Thus, when the potassa of sulphate of potassa, or the potassium of the chloride, became associated with the vegetable organization, we supposed that the salt had been decomposed within the plant, and the sulphuric acid or chlorine eliminated by it. This power does not exist. The salts

* Communicated by Dr. Daubeny.

in question are decomposed by the soil, and the plants all receive their food from elements in the same state of combination.

“The experiments of Way constitute the foundation of a new theory of vegetable nutrition.

“I moreover find that plants living in fresh water receive their food in the very same way as those which are marine. I examined the *lemna trisulca*, which grows on the surface of stagnant water, a plant containing 16·6 per cent. of inorganic matter. I compared the analysis of its ash with that of the water in which the plant had grown, from which it appeared that the plant and the water contain the same constituents, but in very different proportions; thus, the ashes of the plant contained in 100 parts 16·82 of lime, whilst the salts present in the water in 100 parts, contained 35·00.

Again the ashes contain	.	.	5 of magnesia
the salts in the water	.	12	”
the ashes	.	.	13 of potassa
the salts in the water about	.	4	”

“Just then” (as I interpret Baron Liebig’s meaning) “as algæ absorb from sea-water the small quantities of iodine and of potassa present in it, without regard to their amount as compared with other constituents, so the *lemna* appears to do the same with respect to the constituents above cited, a power of selection residing in the roots being in both instances evinced.

“There is perhaps,” continues Baron Liebig, “no mineral spring in the world which contains the amount of soluble salts present in stagnant waters. Compare, for instance, with a mineral spring, the water of the River Thames, that of the springs analysed by Hofmann, Möller, and Graham, and that of the water (drain water) examined by Way, which had drained through soil. Thus, Thames water contains from 1·3 to 7·3 per-centage of potassa, according to the spot from whence it is taken, being richest in potassa where it had received the largest amount of animal matter, as at Lambeth. In well-water the potassa it varies from 0·7 to 6·0 per cent., whilst not more than a trace is found in water which has drained through soil.

“Owing to the cremacausis and decay of the many generations of plants which have existed in stagnant waters, their organic matter is resolved into compounds of oxygen (becomes oxygenated), and their inorganic constituents remain dissolved in the water itself, thus rendering it rich in substances which are never found in equal proportions in the water of springs and rivers.”

Such is the substance of Liebig’s letter to me, with only such alterations as I have thought proper to make in it, in order to render his meaning more intelligible, although in general the Baron’s English style is so good as to require but little correction. In the German paper he has likewise sent me, a

reprint, as I imagine, of an article of his, inserted in the *Allgemeine Zeitung*, more details are given, and some facts added, in corroboration of the views which I have brought before you.

The experiments cited need not, perhaps, detain us, as they do little more than confirm the conclusions arrived at by Professor Way, with which we are already familiar. It does not appear, however, whether he adopts the view at present taken by Mr. Way, namely, that the retention of the alkaline ingredients by the soil is connected with an interchange of elements, the salts of lime, for instance, being carried down with the acid, whilst potassa unites with the carbonic acid set at liberty. Be that, however, as it may, the inference which Liebig draws remains unaffected; for it is evident that, granting this to be the fact, an affinity must be exerted by the soil for the newly-formed salt, in order to prevent its being carried away by the water which percolates through it, and being present in the drainage. Now what is this affinity? Liebig compares it to that which enables charcoal to retain the colouring matter of liquids within its pores, or that which causes starch to unite with iodine; but in any case, something more than the action of water is necessary to overcome it, or the new salts could not remain in the fallow for any time after they had been formed. This assisting force Liebig considers to reside in the roots, and there are certainly many facts which tend to show, that these organs operate, not merely passively, by imbibing any liquid that happens to present itself to them, but that they possess an active, and, as it were, a vital energy, in absorbing some substances, and in eliminating others.

This, indeed, is precisely the same conclusion which I had myself arrived at, so long ago as the year 1833, from experiments in which plants were watered with salts of strontia, without absorbing any appreciable quantity of that earth; as will be seen by my Paper "On the Degree of Solution exercised by Plants with regard to the Earthy Constituents presented to their Absorbing Surfaces," which was published in the Transactions of the Linnean Society for that year.

We may also thus explain, why plants may be watered, as has been done by myself, with weak solutions of arsenic, without being themselves affected, or contracting therefrom any poisonous property; nor is this inconsistent with the fact, that certain poisonous solutions, such as the salts of copper or iron, do find admittance into the tissue of plants, because in these instances the vitality of the roots is in the first instance destroyed, and thus the imbibition of the poison takes place, as would occur even in dead matter, by endosmose and by capillary attraction.

It is at least certain, that the water, which trickles through a bed of soil, contains far too small a proportion of the ingredients which the crop contains, to be regarded as the source from whence

the latter can obtain them, as Baron Liebig has shown by a very simple calculation ; and hence we are driven to attribute them to the constituents which Professor Way's researches have shown to be separated by, and combined with, the soil. Now, as the latter will not impart them to water alone, except in very small quantities, it is at least evident, that some power must reside in the roots, which can assist in overcoming the chemical affinity between the soil and the inorganic matters which the plant assimilates. Such, at least, appears to be the conclusion to which Baron Liebig has arrived, and as no notice seems to have been yet taken of his researches in any English Periodical, I trust I shall be pardoned, both by him and by the Society, in thus bringing forward the substance of a private letter, in which a short abstract of them is contained.

Researches on the Phosphorus-Bases.

By Augustus William Hofmann and Augustus Cahours.

Abstracted from a Paper read before the Royal Society, June 18. 1858.

In a note on the action of chloride of methyl upon phosphide of calcium, communicated more than ten years ago to the Institute of France,* M. Paul Thénard pointed out the existence of a series of bodies which correspond to the compounds of phosphorus with hydrogen, which may, in fact, be viewed as hydrides of phosphorus, the hydrogen of which is replaced by an equivalent quantity of methyl.

One of these bodies, a liquid possessing a most offensive odour, spontaneously inflammable and explosive in the highest degree, corresponds to the liquid phosphoretted hydrogen, and appears to occupy, in the phosphorus-series, the same position which belongs to kakodyl among the arsenic-compounds. It is a colourless, somewhat viscid liquid which boils at about 250°C . Exposed to the slow action of the atmosphere, this liquid is converted into a compound which is strongly acid and easily crystallizes. This acid is probably analogous to kakodylic acid.

In addition to this liquid body, two solid substances are formed by the action of chloride of methyl upon phosphide of calcium. One of these, according to M. Paul Thénard, corresponds to the solid phosphoretted hydrogen, whilst the other, which is the principal product of the reaction, constitutes the hydrochlorate of a very volatile phosphoretted base. From its composition, this body may be viewed as ammonia, in which the nitrogen is replaced by

* Comptes Rendus, t. xxi. p. 144, and t. xxv. p. 892.

phosphorus, whilst methyl is substituted for the hydrogen. When repeating these experiments in the ethyl-series, Paul Thénard arrived at similar results, to which he however only briefly alludes.

At the time when these experiments were first made, the ammonia-bases had not been discovered, and the subject presented obstacles so numerous and varied, that the researches of this chemist remained unfinished. Nobody will be surprised at this, who has made himself acquainted with the difficulty of effecting the above-mentioned reactions, and who, from his own experience knows the danger which attends the preparation of these compounds, and the horrible odour which some of them possess.

Paul Thénard's remarkable researches did not excite, at the time of their publication, that degree of interest which they really deserved. There were but few facts known, at that period, with which his results could naturally be connected; indeed, until after the ammonia-bases were discovered, the importance of the experiments on these phosphorus-bodies could scarcely be recognized; then it was that M. Paul Thénard's investigations attracted that attention to which they were entitled; then it was that the remarkable parallelism of the compounds of phosphorus and nitrogen, more and more distinctly exhibited by these discoveries, began to become an object of general interest to chemists.

It is now many years since M. Paul Thénard abandoned the study of the phosphorus-compounds, for the first knowledge of which we are indebted to him. The unfinished state in which these researches remained, and the rich and abundant harvest collected since that period in all the neighbouring fields of science, necessitated a revision of the subject. The discovery of methylamine, dimethylamine, and trimethylamine, and of the corresponding terms in the ethyl- and amyl-series, had shown that the hydrogen in ammonia may be replaced by binary molecules, such as methyl, ethyl, amyl and phenyl, the newly-formed compounds retaining the basic character of the original ammonia-molecule; whilst the production of triethylstibine and triethylarsine had furnished the proof that the total replacement of the hydrogen in the indifferent antimonietted and arsenietted hydrogen exalts the chemical character of these compounds in a most remarkable manner, the methylated and ethylated bodies exhibiting basic characters scarcely inferior to those of ammonia itself. It remained, therefore, to be investigated, whether phosphorus, which, by its chemical tendencies, stands between nitrogen and arsenic, would exhibit a similar deportment. It remained to be ascertained in what manner the gradual entrance of binary molecules in the place of the hydrogen in phosphoretted hydrogen would change the character of the original compound. The discovery of the tetrethylated ammonium-bases had also opened a new field of research, in which the corresponding terms of the antimony- and

arsenic-series were rapidly brought to light. It was indeed possible to predict with certainty, that an appropriately selected method would lead to the production of the analogous derivatives of phosphoretted hydrogen. The time for resuming the study of the phosphorus-bases had in fact arrived.

We have been engaged for a considerable time in the investigation of this subject, and now beg to offer to the Royal Society in the following pages an account of our experiments.

In the first place, we have endeavoured to obtain the bases corresponding to phosphoretted hydrogen, by a method analogous to that followed by M. Paul Thénard.

Recent experience suggested at once the replacement of the gaseous chloride of methyl by the liquid iodide, which is so much more convenient for experiment; and also the substitution, for the phosphide of calcium, of the compound of phosphorus and sodium obtained by the direct union of the elements. On the application of heat, these substances act on one another with great energy, producing combustible and detonating compounds, so that the experiment is not without danger. Often the product of the operation is lost; and if the reaction has taken place without explosion, the separation of the constituents of the very complicated mixture which results can be effected only with the greatest difficulty.

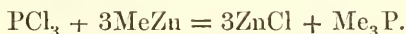
We have convinced ourselves that the product of the action of iodide of methyl upon phosphide of sodium consists chiefly of three different substances, viz, of a liquid which probably is Me_2P , and corresponds to kakodyl; of a second liquid, Me_3P , corresponding to trimethylstibine and trimethylarsine; and lastly, of a beautiful crystalline solid body, Me_4PI , which is the analogue in the phosphorus series of iodide of tetramethylammonium.

We abstain from a minute description of the experiments made in this direction, since in the further course of the inquiry we have forsaken this method altogether. Indeed this mode of preparation is very uncertain, and the separation of the products formed is attended with almost insurmountable obstacles, not to speak of the difficulty of obtaining pure phosphide of sodium fit for the reaction. The question resolved itself into the discovery of a method which would yield us the desired substances conveniently, without danger, in considerable quantity, and in a state of absolute purity.

It appeared to us that the action of terchloride of phosphorus on zinc-methyl, zinc-ethyl, &c., would enable us to attain the desired result. Experiment has fully confirmed this anticipation.

Dr. Frankland's remarkable observations on the action of zinc upon iodide of methyl and iodide of ethyl at high temperatures are still fresh in the memory of chemists. Besides the hydrocarbons methyl and ethyl, zinc-methyl and zinc-ethyl are formed in this reaction, which exhibit the deportment of true organic

metals, comparable in the intensity of their combining powers with the most electro-positive elements. In the action of a chloride upon such a compound metal, the chlorine was sure to seize upon the zinc, and it was extremely probable that, together with chloride of zinc, methyl- or ethyl-compounds would be formed in definite proportions. In the action of terchloride of phosphorus, the formation of a methyl- or ethyl-compound of phosphorus, corresponding in composition to the terchloride of phosphorus, might be with certainty expected :



These anticipations were in fact fulfilled. The products of these reactions, the bases Me_3P and E_3P , which we propose to call respectively trimethylphosphine and triethylphosphine, remain united with chloride of zinc, and simple distillation with an alkali is all that is necessary to liberate them:



They are obtained in this way as volatile oils, with a peculiar and strongly-marked odour, and possessing distinct basic properties.

We found no difficulty in procuring the bodies in question by this method in a state of perfect purity, so as to examine their properties with accuracy.

From the outline which we are about to give, it will be obvious that this group of bodies exhibits the most striking analogies with the ammonia-bases, so much so, in fact, that frequently it will only be necessary to repeat the observations, which were published by one of us about eight years ago, regarding the methylated and ethylated derivatives of ammonia.*

The experiments which we have to communicate refer chiefly to the methyl- and ethyl-compounds; though here and there we have used amyl as material. Since we have preferred working in the ethyl-series, we begin with the description of the ethyl-compounds.

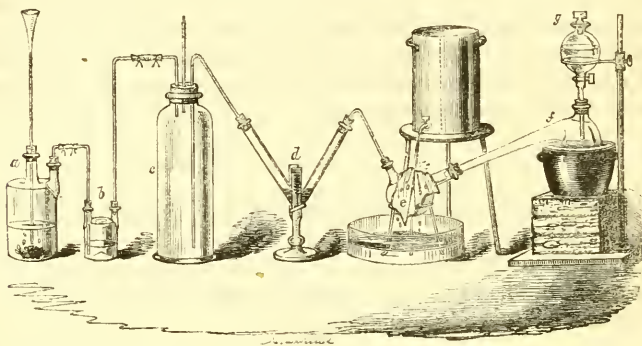
EXPERIMENTS IN THE ETHYL-SERIES.

Action of Terchloride of Phosphorus on Zinc-ethyl.

The reaction between these two bodies is very violent, and readily gives rise to dangerous explosions, if the necessary precautions are neglected. We have generally adopted the following arrangement. A tubulated retort is joined to a receiver which in its turn is connected with a wide glass tube bent at an angle of

* Philosophical Transactions, 1850, p. 93; 1851, p. 357.

about 70° , and acts like a second receiver. The angle of this tube is filled with terchloride of phosphorus, and the tube is connected with a large cylinder which is supplied by a suitable appa-



a. Apparatus for generating carbonic acid. *b.* Wash-bottle containing sulphuric acid. *c.* Reservoir of carbonic acid. *d.* Bent tube containing terchloride of phosphorus. *e.* Receiver. *f.* Retort containing zinc-ethyl. *g.* Dropping apparatus filled with terchloride of phosphorus.

ratus with dry carbonic acid. As soon as the carbonic acid has expelled the air from the reservoir, tube, receiver, and retort, an exit-tube from the reservoir, up to that time closed by a caoutchouc cap, is opened to let out the carbonic acid, the evolution of which is maintained during the whole operation. The tubulature of the retort is now connected with the copper digester in which the zinc-ethyl has been prepared; and as soon as the retort has received a charge of the ethereal solution of zinc-ethyl, there is fixed into the same tubulature a little dropping apparatus, consisting of a glass globe, with a tubulature and stopper at the top, and terminating below in a glass tube in which a stopcock is fitted. This apparatus is filled with terchloride of phosphorus, and by appropriately adjusting the stopcock and opening or closing the stopper of the glass globe, any desired flow of the fluid can be maintained with the greatest nicety.

However slowly the action may be accomplished, and however well, moreover, the retort and receiver may be cooled by water or ice, the action is nevertheless invariably so violent, that all the ether, and with it a large quantity of the zinc-ethyl, passes over into the receiver. By the powerful ebullition which periodically ensues, a portion of the vapour is driven even into the bent tube, and a considerable loss of zinc-ethyl is incurred, unless this tube be filled with terchloride of phosphorus, which greedily absorbs every trace of the former compound. This fluid valve, ascending and descending in the tube, in accordance with the progress of the

reaction, regulates the function of the apparatus so perfectly, that the operation, which always takes several hours, when once begun continues by itself. Sometimes the absorption is so violent that the terchloride of phosphorus in the tube is sucked back into the receiver, but even then no loss is to be feared, since the tube is connected with the reservoir filled with carbonic acid.

The first drops of terchloride of phosphorus which fall into the solution of zinc-ethyl, hiss like water when brought in contact with red-hot iron. The action becomes by-and-by less violent, and as soon as an evolution of heat is no longer perceptible, the operation is terminated. There remain in the retort, in the receiver, in the bent tube, and sometimes even in the carbonic acid reservoir, two liquid layers,—the one a heavy, pale, straw-coloured, thick fluid, the other a transparent, colourless, mobile fluid floating on the former.

The heavy fluid, a compound of the phosphorus-base with chloride of zinc, nearly solidifies on cooling, but the viscid transparent mass exhibits no trace of crystalline structure. The light fluid is a mixture of ether with an excess of the terchloride of phosphorus; after disconnecting the apparatus, it is poured off from the viscous fluid, and may be used, after distillation, in a second operation. Some ether and terchloride of phosphorus which may still adhere are expelled by gently heating the retort upon a sand bath.

In order to liberate the phosphorus-base from its combination with zinc, nothing more than a distillation with potassa is required. To prevent the destruction of the retort, to which the zinc-compound adheres with pertinacity, and the loss of so precious a material, this operation is conveniently performed in the following manner. Solid hydrate of potassa is placed on the hard resinous cake attached to the bottom of the retort, and a slow current of water allowed to flow in by the dropping apparatus, after the air in the retort has been carefully displaced by hydrogen: the heat evolved during the reaction is quite sufficient to volatilize the base with the vapour of the water; it may be condensed by an ordinary cooler. The base, which is now floating on the water of the distillate, is removed by means of a separating funnel; it is allowed to stand for a day over hydrate of potassa, and finally rectified in a current of dry hydrogen gas.

Triethylphosphine.—Thus obtained, triethylphosphine is a colourless, transparent, mobile, liquid, which strongly refracts light. The compound is lighter than water, its specific gravity being found to be 0.812 at 15°.5 C.; it is perfectly insoluble in water, but soluble in every proportion in alcohol and ether. Its odour is penetrating, almost benumbing, but still not disagreeable. The intolerable smell which renders it so unpleasant to work with these phosphorus-compounds, generally arises from other products, which make their appearance in considerable quantities, especially in preparing

the phosphorus-base by means of phosphide of sodium and iodide of ethyl. In a diluted state, the odour of the pure triethylphosphine has the greatest similarity to that of the hyacinth.* Long-continued working with this substance causes headache and sleeplessness.

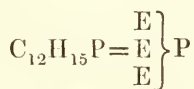
The boiling-point of the triethylphosphine is $127^{\circ}5$ C., under the barometric pressure of 0.744 m. The determination was made with an ounce of the pure substance. The distillation of the phosphorus-base must be performed in a stream of dry hydrogen, for it attracts oxygen with great energy, especially at high temperatures. It is impossible to pour the liquid from one vessel into another without its becoming perceptibly warm. The product of oxidation formed in this way becomes evident in the last stage of the distillation. When the larger quantity of the base has distilled over, the mercury in the thermometer begins suddenly to rise, and before the temperature has become again stationary, the neck of the retort is found to be coated with a network of beautiful crystals, which are even drawn over into the receiver. These crystals are permanent as long as they are protected from the action of the moist air. After disconnecting the apparatus, it is vain to attempt to collect the crystals, the most minute quantity of water causing them to liquefy to a heavy oil, soluble in water. From these remarks, it is obvious that triethylphosphine must be almost always contaminated with a small quantity of this substance; in fact a bottle containing the base cannot be opened without its being formed. When the phosphorus-base is brought in contact with oxygen, vapours are immediately formed; the liquid frequently becomes so hot that it inflames, and the body is burnt with evolution of dense white fumes of phosphoric acid. If a strip of paper, moistened with triethylphosphine, be introduced into a test-tube containing oxygen and immersed in hot water, the vapour of the phosphorus-base produces with the oxygen an explosive mixture, which detonates after a few moments with considerable violence. With atmospheric air a similar detonating mixture is formed, which explodes at comparatively low temperatures. To avoid serious accidents, the phosphorus-base should always be dis-

* There is nothing new in the fact that the odour of a substance may be considerably changed by dilution. Several years ago, when occupied in the preparation of different ethers, which have found numerous applications in perfumery, I had frequent opportunities of observing how the desired aroma, which was absent in the pure substance, was brought out by dilution with alcohol. The hyacinth smell of the dilute phosphorus-base is so characteristic, that one morning I found in my laboratory a large basket filled with hyacinths, the present of a lady friend of mine, who, interested in my labours, had a strong impression that triethylphosphine must be present in the hyacinth. In the interest of science, the entire floral adornment of the garden had been unmercifully sacrificed! It would have been ungrateful not to distil them, but I regret to say, that the anticipation of the amiable donor, who wished to enrich me with so interesting a discovery, proved unfounded. The hyacinth does not contain any phosphorus-base.—A. W. H.

tilled in an atmosphere of hydrogen. When poured into a flask filled with chlorine gas, every drop of triethylphosphine is inflamed with disengagement of pentachloride of phosphorus and hydrochloric acid, and separation of carbon. The phosphorus-base unites with bromine and iodine, evolving considerable heat, which may give rise to inflammation; but if the action be moderated, crystalline compounds are produced. In cyanogen gas the phosphorus-base is converted into a brown resinous mass. If a piece of sulphur be thrown into a test-tube containing triethylphosphine, it becomes so hot as to fuse the sulphur, which then floats on the liquid base in the form of globules, as sodium does on water, and at last entirely disappears. The clear liquid thus obtained, solidifies on cooling to a magnificent crystalline mass. The experiment must be made with caution, since the vapour of the phosphorus-compound, which rises during the reaction, generally explodes on coming in contact with the air contained in the vessel. Selenium gives rise to similar but less powerful phenomena.

Although triethylphosphine, in its relations to other bodies, possesses all the characters of a well-defined base, it does not exhibit an alkaline reaction. When freshly prepared, it is without action on vegetable colours, but when exposed only for a few moments to the influence of the air, it begins to show a constantly increasing acid reaction. Triethylphosphine unites with acids slowly, but with considerable evolution of heat; with concentrated acid the temperature frequently rises to such a degree as to give rise to inflammation of the liquid. Most of its salts are crystalline compounds, but are very soluble and deliquescent.

The composition of triethylphosphine* is represented by the formula

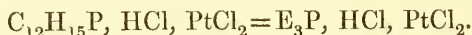


Triethylphosphine forms crystalline compounds with the hydrogen-acids of chlorine, bromine, and iodine, with sulphuric and nitric acids; but all these salts, which can be obtained in the dry state only by the aid of the exsiccator, are but little suitable for analysis. The solution in hydrochloric acid affords a crystalline platinum-salt, which is insoluble in cold water, in alcohol and ether, but which, on account of the facility with which it decomposes at 100° C., must be dried in the exsiccator. In the water-bath it fuses and is altogether decomposed. The determination of the platinum in the phosphorus-compounds presents considerable

* The analytical details are given in the original paper published in the *Philosophical Transactions* for 1857, p. 575.

difficulties. The platinum in these substances cannot be determined in the ordinary way by simple ignition, because a considerable quantity of platinum is carried off with the phosphorus-vapour, however slowly and carefully the process may be carried out. We unfortunately did not find this out, until a great number of unsuccessful analyses had been made. By heating with a considerable excess of carbonate of sodium in a porcelain crucible on a sand-bath, the temperature of which is gradually raised, the determination succeeds without difficulty. After removal of the portion soluble in water, the platinum-residue, which is always contaminated with silicic acid, is dissolved in nitrohydrochloric acid, the solution evaporated to dryness, and the residue again dissolved in acid: the careful evaporation of this solution furnishes a perfectly accurate result. This method is somewhat tedious, but there is some compensation for this increased complexity by the simultaneous determination of the chlorine.

The analysis of the platinum-salt of triethylphosphine has led to the formula

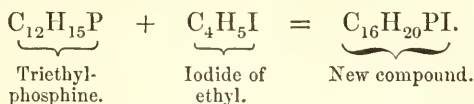


The analyses of the base itself and of the platinum-salt sufficiently fix the composition of triethylphosphine. This compound is in fact triethylamine, in which the nitrogen is replaced by an equivalent quantity of phosphorus. The perfect analogy with triethylamine is also shown by the deportment of the phosphorus-base with the iodides of ethyl, methyl and amyl. Triethylphosphine combines with these substances, forming well-crystallized and highly characteristic salts, which may be regarded as iodide of ammonium, in which the nitrogen is replaced by phosphorus and the hydrogen by the radicals of the alcohols.

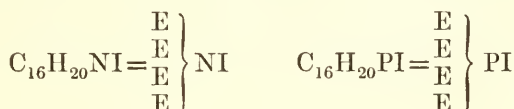
Iodide of Tetrethylphosphonium.—On mixing triethylphosphine with iodide of ethyl, a violent action ensues after a few moments; the liquid effervesces with almost explosive violence, and then solidifies to a white crystalline mass. If, instead of the pure base, an ethereal solution be employed, the crystals are formed more slowly. This new compound is extremely soluble in water, less so in alcohol, and insoluble in ether. The aqueous solution crystallizes on addition of potassa-solution, in which this compound, like the iodides of tetramethylammonium and tetrethylammonium, is but slightly soluble. From the alcoholic solution the salt falls, on addition of ether, as a crystalline powder. If ether be added to a cold alcoholic solution, as long as the precipitate first produced is dissolved by boiling, well-formed crystals of the iodide are deposited on cooling.

The mode of formation and the analysis leave no doubt respecting

the nature of these crystals. They contain the elements of 1 equiv. of triethylphosphine and 1 equiv. of iodide of ethyl.

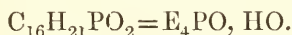


The new body corresponds to iodide of tetrethyl-ammonium.



Notwithstanding the transparency of the constitution of these compounds, we feel some embarrassment in fixing their nomenclature. We propose to designate the hypothetical compound of one equivalent of phosphorus and four equivalents of ethyl by the name "Tetrethylphosphonium." This term is long, but it leaves no doubt regarding the composition of the body, and marks at the same time its analogy with tetrethylammonium. The iodine-compound is accordingly the iodide of tetrethylphosphonium.

Hydrated Oxide of Tetrethylphosphonium.—The separation of the iodine from the before-mentioned compound, presents no difficulties. Oxide of silver removes this element even at the common temperature. A strongly alkaline solution is obtained which retains a small quantity of silver in solution. This liquid, which is almost without odour, and has a bitter and phosphoric taste, dries up, when placed over sulphuric acid, into a crystalline, extremely deliquescent mass, the silver separating at the same time in the form of a black powder, or as a brilliant metallic mirror. The mass, when redissolved in water, furnishes a colourless liquid free from silver, but generally containing some carbonic acid. The avidity with which the oxide of tetrethylphosphonium attracts both water and carbonic acid, has prevented us from analysing this body, but its formation, the composition of the corresponding iodide, and the analyses of a platinum- and gold-salt, hereafter to be mentioned, sufficiently warrant the formula



In its deportment with other substances, the body in question resembles the oxide of tetrethylammonium; we refer therefore to the detailed description which one of us has given of this compound in a former memoir.* The solution of the oxide of tetrethylphosphonium shows in fact all the reactions of a solution of

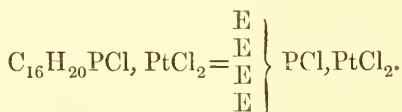
* Journal of the Chemical Society, vol. 4, p. 304.

potassa; the precipitates, such as alumina and protoxide of zinc, dissolve, however, less readily in excess of the phosphorus-compound. The action of heat upon this body gives rise to a peculiar transformation, to which we shall return hereafter.

Tetrethylphosphonium produces crystallizable salts with hydrochloric, nitric, and sulphuric acids. All these compounds exhibit the deliquescent character of the oxide. Like the latter, they are also soluble in alcohol; in ether they are for the most part insoluble. The hydrochloric solution furnishes, with bichloride of platinum and terchloride of gold, difficultly soluble precipitates, which are well adapted for analysis.

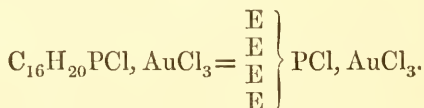
Chloride of Tetrethylphosphonium and Bichloride of Platinum.—The pale orange-yellow precipitate which falls on addition of bichloride of platinum to a moderately dilute solution of the chloride, dissolves with difficulty, but without decomposition, in boiling water; it is insoluble in alcohol and in ether. It can be dried at 100° C.

Formula



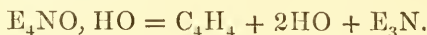
Chloride of Tetrethylphosphonium and Terchloride of Gold.—The crystalline precipitate, obtained by mixing the two solutions, separates from boiling water in brilliant golden-yellow needles.

Formula



ACTION OF HEAT UPON OXIDE OF TETRETHYLPHOSPHONIUM.

The change which oxide of tetrethylammonium undergoes by the action of heat is well known; this body splits into olefiant gas, water, and triethylamine:



We expected an analogous transformation of oxide of tetrethylphosphonium, but experiment has proved that this body suffers a different decomposition. On submitting freshly-prepared oxide of tetrethylphosphonium to distillation, water only passes over in the first instance; but as soon as the solution has attained a certain state of concentration, it suddenly effervesces, with evolution of an inflammable gas which may be collected over water. This gas contains carbon and hydrogen, but no phosphorus; it may be left

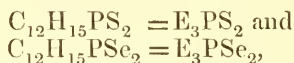
in contact with bromine-water without experiencing the slightest absorption. This experiment shows that the gas cannot contain any ethylene, and with almost the same certainty we may infer the absence in it of all the hydrocarbons of the formula C_nH_n . The evolution of gas ceases long before the whole amount of the liquid contained in the retort has distilled over. On the contrary, it is observed that immediately after the evolution of gas has ceased, the distillation nearly stops, and commences again only when the temperature has reached 200° ; a viscid, nearly inodorous liquid now distils over, the temperature slowly rising, until at about 240° a constant boiling-point is attained: what now distils, generally solidifies to a radiated crystalline mass in the neck of the retort. On fusing this mass with a spirit-lamp, and collecting the liquid in a receiver, it frequently resolidifies instantaneously on cooling; often, however, it remains liquid for months. This body is extremely deliquescent: a crystal exposed to the air only for a few seconds liquefies entirely. It is soluble in water in every proportion, also in alcohol, less so in ether. The aqueous solution is precipitated by potassa; the dissolved body separates in this case in colourless oily drops, which remain liquid even after much concentration, and rapidly dissolve again on diluting the potassa solution with a comparatively small quantity of water. Acids dissolve the oil likewise with facility.

It is obvious at a glance, that the body in question is identical with the product formed by the action of air upon triethylphosphine. A careful comparison of the properties of the two substances places their identity beyond any doubt. It is, moreover, easily proved that the body is a product of oxidation. On boiling triethylphosphine with moderately strong nitric acid, and adding potassa to the highly concentrated liquid, the characteristic oily drops are immediately separated, and disappear again upon addition of water. At the common temperature, oxide of mercury is without action upon triethylphosphine; but on gently warming the mixture, a considerable evolution of heat takes place, metallic mercury is separated, and an oily substance produced which has all the characters of the new compound, and often sublimates in radiated crystals, coating the colder part of the vessel. With oxide of silver exactly the same phenomena are observed. On the other hand, the oily body, when submitted to the action of potassium, instantaneously reproduces triethylphosphine.

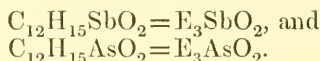
It is difficult to obtain this body in a state fit for analysis. It is not affected by solid hydrate of potassa, but on distilling the two substances together, the distillate is nevertheless found to contain a certain amount of moisture, the hydrate of potassa losing a certain quantity of water at the temperature of distillation. If the crystalline mass be separated from the potassa before distillation, it attracts so much water during manipulation, that even now it

becomes but imperfectly crystalline after distillation. Distillation with anhydrous phosphoric acid furnishes the compound perfectly dry and solid; unfortunately, however, a portion of the substance is thus decomposed, with separation of free phosphorus which contaminates the distillate. Nor have we succeeded in uniting this substance to crystalline combinations; nitrate of silver, bichloride of platinum, and several other reagents were tried in vain.

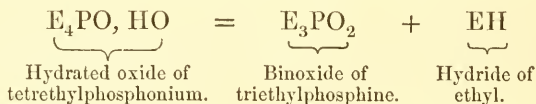
It is obvious that the preparation of this body in a state of purity is attended with unusual difficulties. These difficulties might certainly have been surmounted, but we believe that the deportment of triethylphosphine with sulphur and selenium, which will be more minutely described hereafter, enables us to infer retrospectively the composition of the oxide with a degree of certainty scarcely inferior to that furnished by analysis itself. The examination of well-defined sulphur- and selenium-compounds of the composition respectively



sufficiently proves that the body in question is the corresponding oxide, that it is in fact a combination of triethylphosphine with 2 equivalents of oxygen, $\text{C}_{12}\text{H}_{15}\text{PO}_2 = \text{E}_3\text{PO}_2$; an inference which is moreover supported by the existence of analogous and similarly formed combinations in the antimony- and arsenic-series, viz.

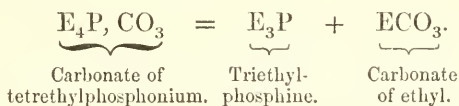


The formation of such a binoxide by the distillation of the hydrated oxide of tetrethylphosphonium, is readily intelligible, if we assume that the hydrocarbon simultaneously disengaged consists of hydride of ethyl, an assumption which is in accordance with the general characters of this gas.



We should have liked to establish this equation by some analytical numbers, but after some fruitless trials to prepare the substance in a state of purity, we were obliged to desist from the attempt. Even the preparation of a considerable quantity of oxide of tetrethylphosphonium is a long, laborious and expensive operation; but to these numerous impediments a further difficulty is added, which at the first glance appeared altogether inexplicable. Under certain conditions, the distillation of oxide of tetrethylphosphonium furnishes either no inflammable gas at all, or only traces; at the same time, the formation of the crystalline binoxide either

entirely ceases, or takes place only in very minute quantities. We have convinced ourselves that this invariably occurs when the alkaline solution, by exposure to the air, has attracted a considerable quantity of carbonic acid. Instead of hydride of ethyl and binoxide of triethylphosphine, the phosphorus-base itself is obtained in this case, together with another liquid body which contains no phosphorus. By dissolving the distillate in ether, fixing the triethylphosphine by sulphur, and then evaporating the ether, an inflammable aromatic liquid remains, which floats on water. We had not more than a few drops of this oil at our disposal, which precluded the idea of an analysis, but we have no doubt that this liquid is carbonate of ethyl.



Chloride, Bromide, and Iodide of Triethylphosphine.—Binoxide of triethylphosphine, when treated with hydrochloric, hydrobromic and hydriodic acids, is converted into the corresponding chloride, bromide, and iodide, which closely resemble the oxide in their general properties. They are liquids which gradually solidify in the exsiccator; the crystals fuse at 100° and begin to volatilize, although their boiling-point is very high. The compounds of triethylphosphine with chlorine, bromine, and iodine may also be obtained by the action of these elements in aqueous or alcoholic solutions upon the phosphorus-base itself. Both methods, however, furnish products which are difficult to purify.

These compounds, as well as the saline compounds which the oxide of triethylphosphine produces with sulphuric and nitric acids, and which in the exsiccator, gradually solidify into semi-crystalline masses, have but slightly occupied our attention, because the formation of beautiful sulphur- and selenium-compounds enabled us to gain a sufficiently precise idea regarding the chemical characters of these substances in general.

Bisulphide of Triethylphosphine.—The remarkable phenomena which attend the combination of triethylphosphine with sulphur have been already described. The compound is likewise obtained by distilling triethylphosphine with cinnabar, which in this reaction is reduced to subsulphide or to metallic mercury. Treatment of the oxide of triethylphosphine with sulphuretted hydrogen or with sulphide of ammonium does not furnish the compound.

The best mode of preparing this beautiful body is the following: Flowers of sulphur are gradually introduced into a dilute solution of the phosphorus-base in ether; the liquid effervesces upon each addition, and the sulphur disappears. As soon as sulphur remaining undissolved indicates the completion of the reaction, the ether

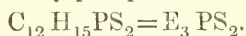
is volatilized, and the residuary mixture of free sulphur and bisulphide of triethylphosphine separated by boiling water. On cooling, the liquid deposits the compound in crystals of perfect purity. This sulphur-compound is one of the finest products with which we have become acquainted in the course of our inquiries. Its crystallizing power is such, that by slowly cooling the solution, most beautiful crystals may be obtained, even in a test-tube, the liquid column being traversed by an aggregate of thin vertical needles, of five or six inches in length. The difference of the solubility of the compound in cold and boiling water is very great; indeed, but a minute quantity remains in solution at the common temperature. On adding an alkali to the cold solution, the mixture becomes turbid, and deposits, after a few moments, small crystals. The sulphur-compound in this respect resembles the corresponding oxide, which is likewise less soluble in alkalies than in pure water. This phenomenon is most strikingly observed by adding potassa to a boiling saturated aqueous solution of the bisulphide; it instantaneously separates in clear oily drops, which rapidly solidify into spherical aggregates of crystals as the liquid cools. The compound is even more readily soluble in alcohol and ether, and also crystallizes from these liquids, but less beautifully. The solubility in bisulphide of carbon is almost unlimited; from this solvent it crystallizes imperfectly.

The fusing-point of the bisulphide of triethylphosphine is 94°C ., it resolidifies at 88°C . When heated beyond 100°C . the bisulphide is volatilized, with diffusion of a white vapour of a disagreeable sulphur-odour, which is but slightly perceptible at the common temperature. When heated with a quantity of water insufficient for its solution, the sulphur-compound rises to the surface as a clear transparent oil, which is copiously volatilized with the vapour of water.

The solution of the bisulphide is without action on vegetable colours. The compound nevertheless appears to possess faintly basic properties. It dissolves more readily in hydrochloric acid, especially when concentrated, than in water, and the solution furnishes with bichloride of platinum a yellow precipitate, which however rapidly cakes into a resinous mass, giving indications of decomposition by the separation of bisulphide of platinum, so that it was not adapted for analysis. The sulphur-compound also dissolves in dilute sulphuric and nitric acids; concentrated nitric acid decomposes it; the fuming acid gives rise to a sort of detonation. The aqueous solution of the bisulphide is not affected by acetate of lead, nitrate of silver, or protoxide of mercury, even at the boiling temperature; the alcoholic solution, on the other hand, is instantaneously decomposed with separation of the sulphide of lead, silver, or mercury. The liquid filtered off from the precipitates now contains the oxide of triethylphosphine, either free or in the form of acetate

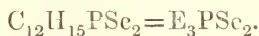
or nitrate, and may be readily separated by the addition of an alkali to the solution. The action of potassium upon this compound instantaneously reproduces the phosphorus-base.

The bisulphide of triethylphosphine has the composition



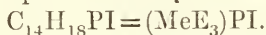
The formation of the bisulphide takes place with such facility, and the properties of the compound are so characteristic, that we have frequently used flowers of sulphur as a reagent for triethylphosphine.

Biselenide of Triethylphosphine.—In the action of selenium upon triethylphosphine, the phenomena described in the preceding paragraphs are repeated. The reaction, however, as might have been expected, is less powerful. The selenium-compound crystallizes from water with the same facility as the sulphur-compound, but the solution is apt to undergo partial decomposition when exposed to the atmosphere. Even the dry crystals are slowly reddened in the air. The fusing point of the selenide is 112°C .; it is easily volatilized, undergoing partial decomposition. It contains

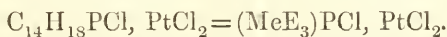


In order to give more completely the history of the phosphorus-bases, we have also examined the compounds which are formed by the action of the iodides of methyl and amyl upon triethylphosphine; but since the products of these reactions resemble in every respect the corresponding ethyl-compounds, we have only to mention the analytical results.

Iodide of Methyltriethylphosphonium.—In treating triethylphosphine with iodide of methyl, all the phenomena mentioned in the case of the analogous experiment with iodide of ethyl are repeated. The action is still more violent and rapid, and if no ether be added, a portion of the product is readily lost by the explosive effervescence of the liquid. The crystals thus obtained contain

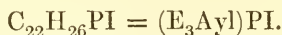


On treating the solution of this compound, which essentially resembles the simple ethyl-compound, with oxide of silver, a strongly alkaline solution of oxide of methyltriethylphosphonium is obtained. The solution, when saturated with hydrochloric acid and mixed with bichloride of platinum, furnishes a beautiful orange-yellow platinum-salt, crystallizing in well-defined cubes, truncated by the planes of the octahedron. This salt, which is insoluble in alcohol and ether, may be recrystallized from boiling water without decomposition; it contains

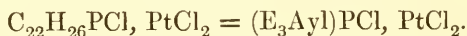


Iodide of Triethylamylphosphonium.—Iodide of amyl acts but

slowly on the phosphorus-base. From a mixture of the two substances in ether, beautiful crystals are deposited after a few days, which may be purified by solution in alcohol and precipitation by ether; they contain

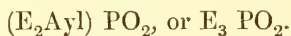


Treatment of this compound with oxide of silver furnishes the free oxide of triethylamylphosphonium, with all the properties characteristic of the class. The corresponding chloride deposits, on addition of bichloride of platinum, a beautiful platinum-salt, crystallizing in prisms, with flat terminal planes. It is insoluble in alcohol and ether, but rather soluble in water. The platinum-salt has the composition

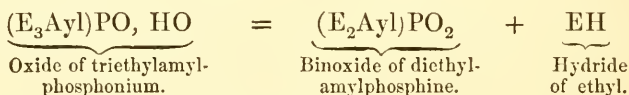


ACTION OF HEAT UPON THE HYDRATED OXIDE OF TRIETHYLAMYLPHOSPHONIUM.

On heating this oxide a small quantity of an inflammable gas is evolved, a liquid being formed at the same time, which boils at about $283^\circ \text{C}.$, and obviously corresponds to the binoxide of triethylphosphine. Two distinct changes may occur in this case. Since the oxide contains several radicals, it is possible that either ethyl or amyl may be eliminated in this decomposition, and the liquid simultaneously generated must therefore contain either



The higher boiling-point of the compound, and the deportment of the corresponding nitrogen-term (the oxide of triethylamylammonium), which on distillation furnishes diethylamylamine together with water and olefiant gas, are in favor of the first assumption. Accordingly, the inflammable gas would also in this case be hydride of ethyl, and the transformation of the oxide of triethylamylphosphonium under the influence of heat would be represented by the equation



Experimentally the question remains undecided.

EXPERIMENTS IN THE METHYL-SERIES.

The results recorded in the preceding sections afford a tolerably complete view of the phosphorus-bases. We may therefore be brief

in describing the experiments which we have made with the methyl-compounds.

Trimethylphosphine.—This remarkable body is obtained by the same process which we have minutely described for the preparation of the corresponding ethyl-base. Zinc-methyl and terchloride of phosphorus furnish the compound of chloride of zinc and trimethylphosphine, from which the base may be expelled by the action of potassa. All the precautions which have been mentioned as necessary in the preparation of the ethyl-base, are required in a higher degree for the methylated body. Since zinc-methyl attracts oxygen even with greater avidity than zinc-ethyl, the current of carbonic acid must be continuously maintained for a long period. The intensity with which zinc-methyl decomposes terchloride of phosphorus, is not inferior to the violent reaction between caustic baryta and anhydrous sulphuric acid. The mixing cannot, therefore, be too slowly effected. In expelling trimethylphosphine from its zinc-compound, refrigeration by ice is absolutely necessary, since this body is far more volatile than the ethyl-base. The distillation must be made in hydrogen gas, and the current of gas must moreover flow very slowly, otherwise, however perfect and careful may be the arrangements for cooling, a considerable quantity of the body will be carried off in the hydrogen and be lost, not to speak of the diffusion of the almost intolerable odor of the methyl-base in the atmosphere of the laboratory.

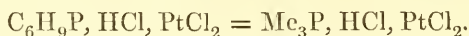
Trimethylphosphine is a colourless, transparent, very mobile liquid of an indescribable odour, powerfully refracting light, lighter than water, in which menstruum it is insoluble. The boiling-point of the liquid lies between 40° and 42° C., which agrees with Paul Thénard's observations. Trimethylphosphine has even a more powerful attraction for oxygen than the corresponding ethyl-base. In contact with the air, it fumes and is apt to be inflamed. On distilling even the freshly prepared methyl-base, the neck of the retort becomes coated in the last stage of the operation with a network of beautiful crystals, perfectly similar to those which are observed with the ethyl-base. These crystals, may be readily obtained in larger quantity by exposing the methyl-base to a slow current of dry atmospheric air. It is scarcely necessary to mention that these crystals are the binoxide of trimethylphosphine.

In its deportment with chlorine, bromine, iodine, sulphur and selenium, and finally with the acids, the methyl-base exactly imitates the ethylated body. The reactions are however more rapid and energetic.

We have been satisfied to identify trimethylphosphine, prepared by means of zinc-methyl, by the analysis of a platinum-salt.

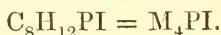
Hydrochlorate of Trimethylphosphine and Bichloride of Platinum.—The solution of the methyl-base in hydrochloric acid, furnishes with bichloride of platinum, an orange yellow, indistinctly crystal-

line precipitate, which, like the corresponding ethyl-compound, is readily decomposed by exposure to 100° C. For analysis it was dried in the exsiccator over sulphuric acid. It contains



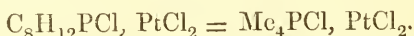
Iodide of Tetramethylphosphonium.—The iodide is a white crystalline mass, obtained by the action of iodide of methyl upon an ethereal solution of triethylphosphine. This compound, which may be readily recrystallized from alcohol, is the finest product of the series. Freshly prepared, it exhibits the silvery lustre of sublimed naphthalin. In contact with the atmosphere it assumes a slightly reddish colour.

The composition of this compound is represented by the formula



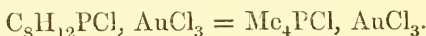
On treating the solution of the iodide with oxide of silver, a very caustic solution of the oxide is obtained.

Chloride of Tetramethylphosphonium and Bichloride of Platinum.—The solution of this oxide, mixed with hydrochloric acid and bichloride of platinum, furnishes a platinum-salt which is insoluble in alcohol and ether, but crystallizes from water in beautiful octahedra. It contains



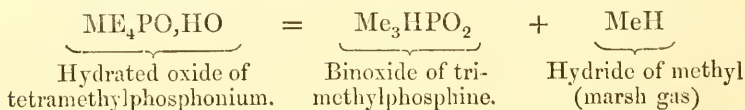
Chloride of Tetramethylphosphonium and Trichloride of Gold.—The method of preparation, and the properties of the gold-salt of chloride of tetramethylphosphonium, are perfectly similar to those of the corresponding ethyl-body.

Formula



ACTION OF HEAT UPON THE HYDRATED OXIDE OF TETRAMETHYLPHOSPHONIUM.

Binoxide of Trimethylphosphine.—Precisely similar phenomena as in the ethyl-series: formation of binoxide of trimethylphosphine and hydride of methyl (marsh-gas).

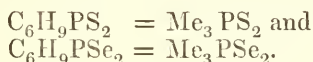


The direct formation of the binoxide by the action of oxygen upon trimethylphosphine has been already mentioned.

Bisulphide and Biselenide of Trimethylphosphine.—These bodies likewise resemble the corresponding members of the ethyl-series; they are, however, more soluble and more volatile. The sulphur-

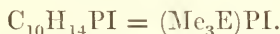
compound crystallizes from a highly concentrated aqueous solution in masses of well-formed four-sided prisms, which fuse at 105°C .

The selenium-compound crystallizes exactly like the ethyl-body; its fusing-point is 84°C . In contact with the air, this compound blackens with separation of selenium. In this decomposition, the characteristic odour of mesitlene is very perceptibly involved. Even without an analysis we may assign to these compounds the formulæ



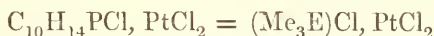
In conclusion, the action of the iodides of ethyl and amyl upon trimethylphosphine may be briefly mentioned.

Iodide of Trimethylethylphosphonium.—This substance is rapidly formed by the action of iodide of ethyl upon the ethereal solution of the methyl-base. The compound, which crystallizes perfectly well from boiling alcohol, contains

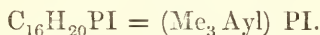


Chloride of Trimethylethylphosphonium and Bichloride of Platinum.—By treating the iodide with oxide of silver, the caustic oxide is obtained, which gives, with hydrochloric acid and bichloride of platinum, a yellow platinum-salt, insoluble in alcohol and ether, but rather soluble in water. From the boiling solution it is deposited in magnificent octahedra.

Formula

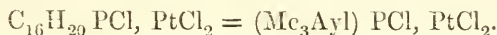


Iodide of Trimethylamylphosphonium.—The ethereal solution of the constituents slowly deposits this compound. It is extremely soluble in water, and hence, if the ethereal solution of the iodide of ethyl contain the most minute trace of water, the salt separates in the form of a syrup, which only gradually solidifies. It crystallizes in needles, although with difficulty, from absolute alcohol. Its composition is



Chloride of Trimethylamylphosphonium and Bichloride of Platinum. This oxide liberated from the iodide by means of oxide of silver, furnishes, with hydrochloric acid and bichloride of platinum, a very soluble platinum-salt, which crystallizes from boiling water in splendid needles, aggregated in spherules.

Formula



The analysis of this platinum-salt concludes the experimental part of our inquiry; for clearness and comparison we subjoin the following synopsis of the compounds which we have investigated.

a. METHYL-SERIES.

Trimethylphosphine	Me_3P .
Platino-chloride of trimethylphosphine	$\text{Me}_3\text{P}, \text{HCl}, \text{PtCl}_2$.
Binoxide of trimethylphosphine	Me_3PO_2 .
Bisulphide of trimethylphosphine	Me_3PS_2 .
Biselenide of trimethylphosphine	Me_3PSe_2 .
Iodide of tetramethylphosphonium	Me_4PI .
Platino-chloride of tetramethylphosphonium	$\text{Me}_4\text{PCl}, \text{PtCl}_2$.
Auro-chloride of tetramethylphosphonium	$\text{Me}_4\text{PCl}, \text{AuCl}_3$.
Iodide of trimethylethylphosphonium	$(\text{Me}_3\text{E})\text{PI}$.
Platino-chloride of trimethylethylphosphonium	$(\text{Me}_3\text{E})\text{PCl}, \text{PtCl}_2$.
Iodide of trimethylamylphosphonium	$(\text{Me}_3\text{Ayl})\text{PI}$.
Platino-chloride of trimethylamylphosphonium	$(\text{Me}_3\text{Ayl})\text{PCl}, \text{PtCl}_2$.

β. ETHYL-SERIES.

Triethylphosphine	E_3P .
Platino-chloride of triethylphosphine	$\text{E}_3\text{P}, \text{HCl}, \text{PtCl}_2$.
Binoxide of triethylphosphine	E_3PO_2 .
Bisulphide of triethylphosphine	E_3PS_2 .
Biselenide of triethylphosphine	E_3PSe_2 .
Iodide of tetrethylphosphonium	E_4PI .
Platino-chloride of tetrethylphosphonium	$\text{E}_4\text{PCl}, \text{PtCl}_2$.
Auro-chloride of tetrethylphosphonium	$\text{E}_4\text{PCl}, \text{AuCl}_3$.
Iodide of methyltriethylphosphonium	$(\text{MeE}_3)\text{PI}$.
Platino-chloride of methyltriethylphosphonium	$(\text{MeE}_3)\text{PCl}, \text{PtCl}_2$.
Iodide of triethylamylphosphonium	$(\text{Ayl E}_3)\text{PI}$.
Platino-chloride of triethylamylphosphonium	$(\text{Ayl E}_3)\text{PCl}, \text{PtCl}_2$.

On glancing once more over the phosphorus-compounds described in the preceding memoir, a comparison of these substances with the corresponding terms of the nitrogen-, arsenic-, and antimony-series is unavoidably forced upon us. Whether we consider the composition, or whether we review the properties of these groups, the most striking analogies, indeed an almost perfect parallelism, cannot be mistaken; the same formulæ, the same mode of combination, the same decompositions.

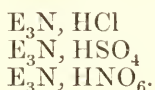
This analogy is particularly manifest in the compounds belonging to the ammonium-type. In these remarkable bodies, nitrogen, phosphorus, arsenic, and antimony appear to play absolutely the same part. It is more especially in the oxides of these compound metals that analogy of composition induces a perfect identity in properties, and, indeed, of very salient properties, which may be traced in almost every direction. If we were satisfied with the study of the reactions of these bodies, we should never suspect, in

compounds exhibiting such a close similarity of properties, the presence of elements so dissimilar as nitrogen, phosphorus, arsenic, and antimony; they might, moreover, be confounded with potassa and soda, by which they are scarcely surpassed in alkaline power. Only the deportment of the hydrated oxides, under the influence of heat, distinguishes the derivatives of nitrogen from the corresponding terms of the phosphorus-arsenic- and antimony-series.

If we regard, on the other hand, the compounds belonging to the ammonia-type, we observe that the electro-positive character of the substances gradually rises in intensity from the nitrogen- to the antimony-compounds.

Thus, trimethylamine and triethylamine are not capable of uniting with oxygen, chlorine, bromine, and iodine; a power which the corresponding terms of the phosphorus-, arsenic-, and antimony-series possess in a high degree.

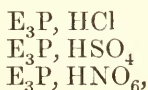
Triethylamine unites with the acids producing compounds of the formula



The corresponding compounds in the arsenic- and antimony-series do not exist; at all events chemists have not yet succeeded in preparing them. Triethylarsine and triethylstibine only combine *directly* with oxygen, chlorine, sulphur, &c., producing saline bodies, which have the composition respectively—



In the phosphorus-series, lastly, the two classes are represented. Triethylphosphine not only forms compounds analogous to the salts of triethylamine, but also the terms corresponding to the binoxides of triethylarsine and triethylstibine. We have in the first place the terms



and in the second place compounds of the formulæ



The phosphorus-compounds accordingly hold a position intermediate between the nitrogen-compounds on the one hand, and

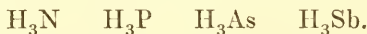
the arsenic- and antimony-series on the other. It cannot, however, be denied that the phosphorus-compounds stand closer to the arsenic- and antimony-series than to the nitrogen-group.

This cannot surprise us, when we consider the close analogies which phosphorus and arsenic present in many other directions. Both phosphorus and arsenic form well-characterized polybasic acids; the acids of antimony are not yet sufficiently investigated, but the acids of nitrogen, which are better examined, are all found to be essentially monobasic. The equivalent numbers, too, of phosphorus, arsenic, and antimony, present a remarkable connection, the difference between those of phosphorus and arsenic, and those of arsenic, and antimony being virtually the same—

Phosphorus	. . .	31	} difference	. . .	44,
Arsenic	75		} difference	. . .
Antimony	120			

whilst the equivalent of nitrogen stands altogether apart from the rest.

The same relative position of the elements nitrogen, phosphorus, arsenic and antimony, may also be traced in their hydrides,



Ammonia is a powerful alkali;—phosphoretted hydrogen only unites with hydrobromic and hydriodic acids, whilst in arseniетted and antimonietted hydrogen, the power of combining with acids has altogether disappeared. In these hydrogen-compounds, the gradation of properties is indeed much more marked than in their trimethylated and triethylated derivatives. On comparing the terminal points of the series, ammonia and antimonietted hydrogen, we cannot fail to be struck by the dissimilarity of properties, which at the first glance, appears to limit the analogy of the two compounds to a mere parallelism of composition.

In the methylated and ethylated derivatives of these compounds, the intensity of the chemical tendencies in general is so much raised, that the gradation is no longer perceptible to the same extent.

We cannot conclude this memoir without thankfully acknowledging the able and untiring assistance we have received, during this lengthened inquiry, from Dr. A. Leibius in the analyses, and from Messrs. W. H. Perkin and C. Hoffmann in the preparation of the numerous compounds which had to be investigated.

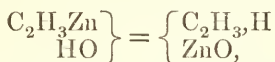
On a New Series of Organic Acids containing Nitrogen.

By E. Frankland, Ph.D., F.R.S., Lecturer on Chemistry at St. Bartholomew's Hospital.*

(Read before the Royal Society, June 19, 1856.)

ABSTRACT.

IN the progress made by Organic Chemistry during the past fifteen years, no generalization has perhaps contributed so extensively to the development of this branch of the science, as the doctrine of substitution. The value of this doctrine becomes even still more apparent, when it is remembered that chemists have, until very recently, possessed adequate means for following out its suggestions, in one direction only. The peculiar habits of chlorine render the substitution of an electro-positive constituent by this element, generally a work of little or no difficulty, and even the like substitution of other electro-negative for electro-positive elements in organic bodies, presents no insurmountable obstacles. But the inverse process has hitherto been successfully accomplished only in comparatively few cases, owing to the want of a body capable, like chlorine, of effecting such a replacement with facility. This want is now supplied in zincmethyl and its homologues; bodies which, on account of their intense affinities and peculiar behaviour, possess in an eminent degree the property of removing electro-negative constituents and replacing them by methyl, ethyl, &c. The action of zincmethyl upon water, attended as it is by the substitution of methyl for oxygen,



may be regarded as the type of these reactions, which open up a most extensive and perfectly new field of research, from the cultivation of which important discoveries cannot fail to spring. Amongst the reactions of this nature which promise most interesting results, are those with the chlorine and oxygen substitution products derived from the ethers and organic acids, which might lead to the higher members of each homologous series being produced from the lower ones, if not to the building up of some of those series from their inorganic types; a discovery which cannot now remain long in abeyance.† Instead of immediately pursuing this line of investigation, however, I determined in the first place to confine my attention to the action of these organo-zinc bodies upon inorganic compounds.

In a former memoir‡ I endeavoured to give a general view of

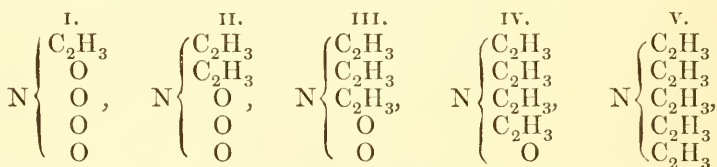
* Phil. Trans., 1857, 59.

† This discovery has since been made by Mr. Wanklyn, who has succeeded in forming propionic acid from carbonic acid by the action of sodium-ethyl upon the latter body.—April, 1858. E. F.

‡ Phil. Trans., 1852, 438.

the rational constitution of all the organo-metallic bodies then known, by showing that they all possessed a molecular isonomy with the inorganic compounds of the respective metals. The only compound which at that time did not coincide with this view was LÖWIG's so-called ethostibylic acid, the formula of which $\text{SbC}_4\text{H}_5\text{O}_5$, I suggested would probably be found to be erroneous*; and in fact, LÖWIG has since announced this to be the case: he now assigns to this compound the formula $\text{Sb}(\text{C}_4\text{H}_5)_3\text{O}_2, 2\text{SbO}_3$, which harmonizes perfectly with the general view I ventured to propound. The recent researches of МЕРСК† upon the compounds of stibethyl, although they probably prove the existence of certain new compounds of this radical, are by no means conclusive as to the non-existence of the bodies originally described by LÖWIG. With regard to those stanethyl compounds which have been since discovered, several of them correspond exactly with the known oxides of tin; the remainder are also by no means irreconcilable with my hypothesis, if we consider the polymeric attributes of stannic acid. Nevertheless, I conceive that the formulæ, and even the existence of some of the more complex stanethyl compounds, require confirmation before these bodies can be employed, either for the support or disproof of any general theory of the rational constitution of organo-metallic compounds.

Taking, then, this view of the organo-metallic compounds as my guide, I pointed out in a former memoir,‡ that the oxygen compounds of nitrogen might probably be represented by corresponding organic compounds, in which one or more equivalents of oxygen were replaced by an organic radical: thus, to take one example, nitric acid, by the substitution of methyl, should yield the following derivatives:—



of which the fourth is already known as oxide of tetramethylammonium. My attempts to produce these derivatives from the oxygen compounds of nitrogen have hitherto been confined to the binoxide, in which I have succeeded in replacing oxygen by ethyl in the manner now to be described.

Action of Zincethyl upon Bin oxide of Nitrogen.

If a small quantity of zincethyl, either pure or dissolved in ether, be passed up into dry bin oxide of nitrogen confined over

* Phil. Trans., 1852, 442.

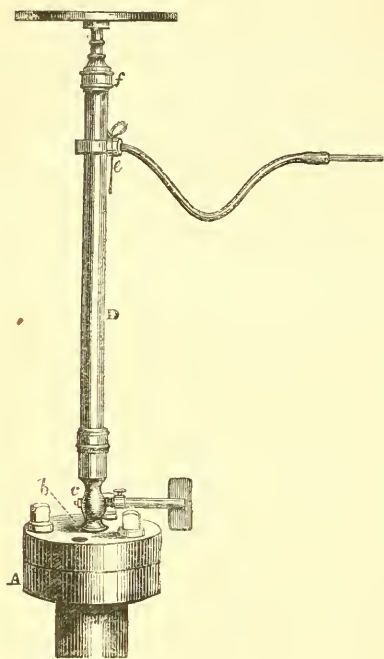
† J. pr. Chem., lxxvi, 56.

‡ Phil. Trans. cxliii; 442.

mercury, the binoxide is very slowly but completely absorbed in large quantity, without the production of any other gas. The solution may be accelerated by agitation, but even then it is exceedingly slow. At the expiration of from one to four days, rhomboidal crystals begin to be deposited, and increase in number until the liquid finally solidifies. To prepare these crystals in larger quantity, about an ounce of zincethyl, dissolved in an equal bulk of dry ether, was placed in a flat-bottomed flask and supplied with binoxide of nitrogen from a gas holder, the gas being thoroughly dried, by bubbling through a long series of bulbs filled with concentrated sulphuric acid, which also served to absorb any traces of nitrous gas that might be formed by atmospheric oxygen gaining access to the interior of the apparatus. The gas was conducted into the flask by a tube which terminated just below the cork; whilst a provision was made for its exit by another tube continued to within a short distance of the surface of the liquid, and which terminated outside the cork in a capillary extremity, that could be readily sealed up by the blowpipe and reopened at pleasure. Binoxide of nitrogen, prepared from copper turnings and nitric acid, always contains a considerable percentage of protoxide, and it was therefore necessary occasionally to allow a stream of the gas to flow through the flask, so as to prevent the absorption being hindered or stopped by the accumulation of protoxide of nitrogen: at other times the exit tube was hermetically sealed, and the gas supplied only as it was absorbed. In this way, although the apparatus was in action day and night, six weeks elapsed before the absorption was completed. On another occasion, when the action was accelerated by violent agitation of the liquid for several hours each day, the zincethyl was saturated in about a fortnight. It was evident that such a process was little calculated for the production of considerable quantities of the new compound, and recourse was therefore had to mechanical means in order to expedite and facilitate the operation. Fig. 1 is from a photograph of the apparatus employed for this purpose, and as it will no doubt prove useful in other cases for experiments with sparingly soluble gases, I will describe it somewhat in detail. A is a copper digester similar to the one I have already described for the preparation of zincethyl*; into the aperture *b* is screwed the stopcock *c*, to which can be attached at pleasure the condensing syringe D made of gun-metal, 12 inches long and 0.7 inch in diameter. In this syringe a solid steel piston $1\frac{3}{4}$ inch deep works air-tight, and the piston-rod passes through a stuffing-box *f*. The syringe is supplied with gas through the nozzle *e*, to which a flexible tube is attached. When the stopcock *c* is

* Phil. Trans., cxlv, 261.

closed, the elevation of the piston produces a vacuum, which is instantly filled with gas, so soon as the piston has passed the nozzle *e*. Between *e* and *f* the interior of the syringe is grooved longitudinally, so as to prevent any compression of gas behind the piston, when it is drawn up to *f*. On forcing down the piston and opening the stopcock *c*, it is obvious that the gas occupying the syringe from *e* to *c* will be forced into A. By repeating this process, it is not difficult for a single operator to compress about twenty atmospheres into A; such a degree of compression exerting upon the piston a pressure of about 114 lbs.



In each operation about three ounces of zincethyl in ethereal solution was placed in the copper cylinder A, and the condensing syringe being attached, about twenty atmospheres of dry binoxide of

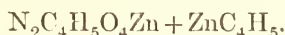
nitrogen were introduced; the syringe was unscrewed and the the cylinder A agitated for two or three minutes by rolling upon the floor or otherwise; at the end of which operation, the pressure within A was found to be reduced to three or four atmospheres; the process of condensation and agitation being repeated five or six times, the copper cylinder becomes so much heated as to require immersion in cold water for a few minutes. At this stage of the process it is also desirable to allow the residual gas in A to escape.

This residual gas consists principally of protoxide of nitrogen and hydride of ethyl; the latter derived from the decomposition of zincethyl by a trace of aqueous vapour introduced with the binoxide of nitrogen. By repeating the above series of operations six or eight times, the zincethyl becomes saturated and the process is completed. If it be desired to obtain the crystalline compound in a state of perfect purity, it is better to place the zincethyl in a wide glass tube open at top and fitting into A; but in this case very moderate agitation only can be used, and consequently the absorption takes place more slowly, and the operation requires two or

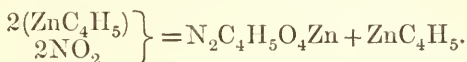
three days for its completion. It is, however, rarely necessary to have recourse to this modification of the process.

At the conclusion of an operation conducted as above, with the intervention of a glass tube, the contents of the latter consisted of a mass of colourless crystals immersed in an ethereal solution; the latter was poured off and the former were freed from ether, by plunging the tube in a water-bath at 90° C. and passing through it a stream of dry carbonic acid. The resulting crystalline mass attracted oxygen from the air with such avidity, as to burst into flame when any considerable quantity was freely exposed; it was also instantly decomposed by water, and was therefore transferred at once into small glass tubes, which were then immediately sealed hermetically.

The results of the analyses prove that the new body is formed by the union of an equal number of atoms of zincethyl and binoxide of nitrogen; but from considerations given below, the above formula requires to be doubled, and I shall presently show that the body is a compound of zincethyl with the zinc salt of a new acid, for which I propose the name *Dinitroethylic acid*. Its formula is therefore



This compound is produced from zincethyl and binoxide of nitrogen, according to the following equation:—



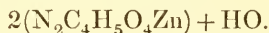
Dinitroethylate of zinc and zincethyl is deposited from its ethereal solution in large colourless and transparent rhomboidal crystals, which instantly become opaque on exposure to the air, owing to the formation of an oxidized product. These crystals are tolerably soluble in anhydrous ether without decomposition, but they are instantly decomposed by anhydrous alcohol and by water. Exposed to the gradually increasing heat of an oil-bath, dinitroethylate of zinc and zincethyl fuses at 100° C., froths up and begins slowly to evolve gas. At 180° C. the colour darkens, and a small quantity of a yellowish liquid of a penetrating odour, free from zincethyl, and possessing a very powerful alkaline reaction, distils over. This liquid, neutralized with hydrochloric acid and treated with bichloride of platinum, yielded a splendidly crystalline platinum salt, which was obtained, however, in too small quantity to allow of its composition being determined. From 180° to 190° C., dinitroethylate of zinc and zincethyl evolved gas very rapidly, and the experiment was then interrupted. The gas consisted of 18·4 per cent. carbonic acid, 23·66 per cent. olefiant gas, and 57·94 per cent. of a mixture of hydride of ethyl, nitrogen, and protoxide of nitrogen.

When brought into contact with water, dinitroethylate of zinc and zincethyl is immediately decomposed with lively effervescence. A large quantity of inflammable gas is evolved, and a white flocculent substance formed. At the conclusion of the reaction, the latter dissolves almost completely, forming an opalescent solution resembling milk, possessing a powerfully alkaline reaction and a peculiarly bitter taste.

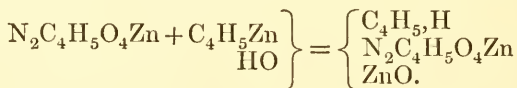
In order to ascertain the exact nature of the gas evolved in this reaction, some crystals of dinitroethylate of zinc and zincethyl were passed up into an inverted receiver filled with mercury, and were then brought into contact with a small quantity of water. The gas thus collected over mercury possessed an ethereal odour, burnt with a slightly luminous flame, and was completely soluble in an equal volume of alcohol. It was perfectly neutral, and underwent no change on being treated successively with caustic potash solution and dilute sulphuric acid.

The specific gravity of the gas was found to be 1.0515, which, together with the results of its eudiometrical analysis, show it to be pure hydride of ethyl.

On submitting the milky solution, formed by the decomposition of dinitroethylate of zinc and zincethyl in water, to a stream of carbonic acid, a copious precipitate of carbonate of zinc, free from organic matter, was thrown down: the liquid was then heated to boiling and filtered. The filtrate, evaporated almost to dryness in a water-bath, yielded a white, radiated, crystalline mass, which, after being reduced to powder, pressed between blotting-paper, and dried over sulphuric acid, was submitted to analysis, the results of which correspond with the formula



The composition of this body proves that the action of water upon dinitroethylate of zinc and zincethyl consists in the transformation of the zincethyl into oxide of zinc and hydride of ethyl, thus

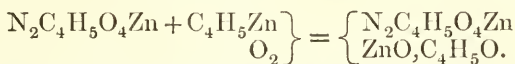


The neutral dinitroethylate of zinc, however, thus set at liberty, immediately unites with a second equivalent of oxide of zinc, to form the basic salt $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Zn} + \text{ZnO}$, which is decomposed by carbonic acid into carbonate of zinc and the neutral salt.

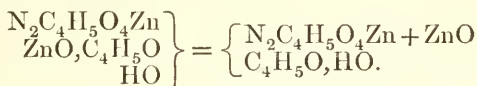
Dinitroethylate of zinc crystallizes with half an equivalent of water, which is expelled at 100°C ., the loss in drying being 3.98 per cent. and 3.75 per cent. respectively, whilst the theoretical number is 3.57.

Dinitroethylate of zinc is also produced by the direct oxidation

of dinitroethylate of zinc and zincethyl in a stream of dry air, ethylate of zinc being at the same time formed: the completion of the oxidation is known by the product ceasing to effervesce in contact with water. This reaction is expressed by the following equation:—



When this product is treated with water, alcohol and bibasic dinitroethylate of zinc are produced,



One of the equivalents of base being removed by carbonic acid, the filtered solution of the neutral salt thus obtained was evaporated to crystallization, and the crystals heated to 100° for some time; at this temperature they fused and afterwards solidified in cooling to a gummy mass, which analysis proved to be the anhydrous dinitroethylate of zinc.

Finally, dinitroethylate of zinc and zincethyl is produced by adding an ethereal solution of zincethyl to anhydrous dinitroethylate of zinc, and corresponding compounds appear to be formed under similar circumstances, with other salts of dinitroethylic acid. These compounds are evidently of the same nature as that produced by the union of zincethyl with iodide of zinc, which is formed in such large quantity during the preparation of zincethyl.

Dinitroethylate of zinc crystallizes in minute colourless needles containing half an equivalent of water, which they retain when exposed over sulphuric acid *in vacuo*. They fuse below 100° C., and gradually become anhydrous at this temperature. They are very soluble in water and in alcohol. The concentrated aqueous solution solidifies on cooling to a white fibrous crystalline mass. Heated suddenly in air to a temperature of about 300°, this salt does not deflagrate, but it inflames, burning rapidly with a beautiful bluish-green flame. When dry dinitroethylate of zinc is treated with concentrated sulphuric acid, and the vessel containing those ingredients is placed in a freezing mixture, dinitroethylic acid is liberated; but it is so unstable, that when the temperature rises a few degrees, it begins to effervesce violently, and is rapidly decomposed with evolution of gases and white vapours. A dilute solution is somewhat more stable; it may be prepared, either by decomposing a dilute solution of dinitroethylate of zinc with dilute sulphuric acid and then distilling *in vacuo*, or by adding to a dilute solution of the baryta salt just sufficient sulphuric acid to precipitate the base. Dilute dinitroethylic acid thus prepared possesses a pungent odour, somewhat resembling that of the nitro-

fatty acids, and an acid taste. It reddens litmus-paper strongly and gradually decomposes, even at ordinary temperatures.

The acid procured by distillation *in vacuo* being treated with carbonate of silver, the latter dissolved with evolution of carbonic acid. The filtered solution, evaporated over sulphuric acid, deposited light flocculent crystals of dinitroethylate of silver, which blackened rapidly. They gave, by treatment with nitric acid and subsequent ignition, 55.85 per cent. of metallic silver. The formula $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ag}$ requires 54.82 per cent. Another portion of the dilute acid, procured by the decomposition of the baryta-salt as described above, was saturated with magnesia, evaporated to dryness, and the residue treated with strong alcohol. The filtered alcoholic solution, which contained no trace of sulphuric acid, gave, on evaporation, dinitroethylate of magnesia, which, by treatment with nitric acid and ignition, yielded 19.64 per cent. of magnesia. The formula $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Mg}$ requires 19.80 per cent.

The salts of dinitroethylic acid are all soluble in water and alcohol, and most of them crystallize with more or less difficulty. They are all violently acted upon by concentrated nitric acid, the dinitroethylic acid being entirely decomposed and a nitrate of the constituent base produced. Dilute nitric acid acts in the same manner, but more slowly. They all fuse at a temperature a little above 100°C . The potash, soda, lime, and baryta-salts deflagrate explosively, like loose gunpowder, at a temperature considerably below redness.

Dinitroethylate of Baryta.— $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ba}$. This salt is produced by adding caustic baryta in excess to a solution of dinitroethylate of zinc, carbonic acid being passed through the solution until the excess of baryta is precipitated. It is then treated with sulphuretted hydrogen to remove a trace of oxide of zinc, which is still held in solution. After being heated to boiling for a few minutes, and then filtered, the solution is concentrated by evaporation, and finally dried down to a gummy mass, which does not crystallize on cooling. This is anhydrous dinitroethylate of baryta.

Dinitroethylate of baryta is uncrystallizable, very deliquescent, and very soluble in water. Its solution reacts perfectly neutral.

Dinitroethylic Ether.—Several attempts were made to prepare this compound by the usual methods of etherification, but with only very partial success. When crystallized, dinitroethylate of lime is distilled with sulphovinate of potash, alcohol comes over mixed with an ethereal liquid which dissolves in water, but separates again on the addition of chloride of calcium, in the form of oily drops of a peculiar ethereal odour. I only succeeded, however, in obtaining such minute quantities of this body, as to preclude the possibility of fixing its composition.

Dinitroethylate of Lime.— $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ca} + 3\text{HO}$. This salt is readily prepared by treating solution of dinitroethylate of zinc with excess of hydrate of lime, passing carbonic acid through the solution, and then heating to boiling for a few minutes. The filtered solution deposits, on evaporation, beautiful silky needles of dinitroethylate of lime, which contain three atoms of water, two of which are expelled at 100°C . An estimation of lime in this salt gave 20.76 per cent.; the above formula requires 20.59 per cent.

Dinitroethylate of Silver is produced by double decomposition from dinitroethylate of baryta and sulphate of silver. It is very soluble in water, crystallizes in very light scales, and is so speedily decomposed, even with little exposure to light, that no satisfactory analysis could be made.

Double Nitrate and Dinitroethylate of Silver.— $\text{AgONO}_5 + \text{AgON}_2\text{C}_4\text{H}_5\text{O}_3$. This salt is very sparingly soluble in water; it is precipitated in a crystalline granular form when concentrated solutions of dinitroethylate of zinc and nitrate of silver are mixed.

Dinitroethylate of Copper.— $2(\text{N}_2\text{C}_4\text{H}_5\text{CuO}_4) + \text{HO}$. This salt is prepared by mixing solutions of dinitroethylate of baryta and sulphate of copper. The filtered solution is of a magnificent purple colour; on evaporation *in vacuo* it yields splendid purple needles, which contain half an equivalent of water, and may be obtained several inches in length; they are four-sided prisms.

Dinitroethylate of Magnesia, $\text{N}_2\text{C}_4\text{H}_5\text{MgO}_4$.—Prepared by treating the solution of dinitroethylate of zinc with excess of caustic magnesia, boiling and filtering. The filtered solution, concentrated in a water-bath, yielded granular crystals, which fuse at 100°C . and dry up to a solid amorphous mass. This is the anhydrous salt.

Dinitroethylate of Soda, $\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Na}$.—Prepared by precipitating dinitroethylate of lime with carbonate of soda, and evaporating the filtrate in a water-bath. The residue being treated with strong alcohol, the dinitroethylate of soda dissolves, and is thus separated from the excess of carbonate of soda. The alcoholic solution evaporated to dryness in a water-bath, yielded minute scaly crystals, which were anhydrous.

Products of the Decomposition of Dinitroethylic Acid.

I have stated that when dinitroethylic acid is liberated from its salts, by the addition of concentrated sulphuric acid, it is rapidly decomposed, even at 0°C . I have examined the products of this decomposition in the case of the lime-salt, with the following results. A quantity of crystals of dinitroethylate of lime in coarse powder was placed in an apparatus, in which it could be gradually decomposed by concentrated sulphuric acid, the gaseous products collected, and their weight accurately ascertained. The rapidity

of decomposition was moderated by the external application of cold water. At the conclusion of the decomposition, it was found that the weight of the gaseous products evolved was equal to 30·6 per cent. of the weight of the lime-salt employed. The weight of gaseous products is therefore almost exactly one-half of the weight of the anhydrous acid contained in the lime-salt (59·6 per cent.). The liquid and solid products of the operation contained sulphate of lime, sulphovinate of lime, and sulphate of ammonia or ethylamine. These gaseous products, after streaming through concentrated sulphuric acid, were collected over mercury and submitted to eudiometrical investigation. The specific gravity was found to be 1·3601.

The mean percentage composition of the gas, was:

Binoxide of nitrogen	.	.	.	8·90
Olefiant gas	.	.	.	24·24
Protoxide of nitrogen	.	.	.	60·65
Nitrogen	.	.	.	6·21
				<hr/>
				100·0

This result is confirmed by the specific gravity of the gas, as is seen from the following calculations:—

	Per cent.	Specific	
	amount.	gravity.	
Binoxide of nitrogen . . .	8·90	$\times 1·0365 =$	9·2249
Protoxide of nitrogen . . .	60·65	$\times 1·5202 =$	92·2001
Nitrogen . . .	6·21	$\times \cdot 9674 =$	29·4573
Olefiant gas . . .	24·24		
	<hr/>		130·8823
	100·00		<hr/>
			100
			<hr/>
			= 1·3088

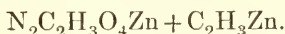
Found by experiment 1·3601

I had anticipated that the decomposition of dinitroethylate of lime by sulphuric acid would yield either protoethide of nitrogen (NC_4H_5) or ethoprotoxide of nitrogen ($\text{NC}_4\text{H}_5\text{O}$), but the action of the concentrated acid evidently proceeds too far for the production of this result. Further experiments must decide whether or not the employment of a more dilute acid for the decomposition will lead to the production of one of these compounds.

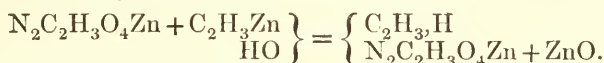
Action of Zincmethyl upon Binoxide of Nitrogen.

Dinitromethylate of Zinc and Zincmethyl.—Zincmethyl absorbs binoxide of nitrogen much more slowly than zincethyl takes up the same gas; nevertheless at the ordinary atmospheric pressure, the two bodies gradually unite and form colourless crystalline needles, closely resembling, in all their reactions, the dinitroethylate of zinc and zincethyl. I have made no analyses of this body, but

considering the homology existing between zincethyl and zincmethyl, together with the product of its decomposition by water, there can scarcely be a doubt that it is dinitromethylate of zinc and zincmethyl, and that its formula is



It rapidly oxidizes in the air, and takes fire when exposed in considerable quantity. It is instantly decomposed by water, giving light carburetted hydrogen and an opalescent solution of basic dinitromethylate of zinc.

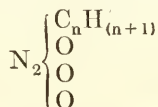


Dinitromethylate of Zinc, $\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{Zn} + \text{HO}$.—A quantity of the dinitromethylate of zinc and zincmethyl was prepared by the action of compressed binocide of nitrogen upon zincmethyl, in the strong copper vessel above described. The resulting crystalline compound was decomposed by water, and the opalescent solution being treated with carbonic acid, boiled, and filtered, yielded, on evaporation, minute crystals of dinitromethylate of zinc.

Dinitromethylate of Soda, $\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{Na} + 2\text{HO}$.—This salt is formed by treating a solution of dinitromethylate of zinc with carbonate of soda, evaporating to dryness, and treating the residue with strong alcohol. Dinitromethylate of soda dissolves, and the filtered solution, on evaporation, deposits crystals, which, after drying at 100°C ., yielded 25.83 per cent. of soda; the above formula requires 26.72 per cent. Dinitromethylate of soda, is very soluble both in water and alcohol; it deflagrates violently when heated, and in other respects closely resembles the corresponding salt of dinitroethylie acid.

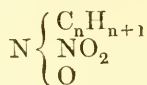
These determinations, although very imperfect and incomplete, establish the existence of a class of salts containing dinitromethylie acid, homologous with the dinitroethylates; and there can be little doubt that the zinc compounds of the other alcohol-radicals will yield corresponding acids, when treated with binocide of nitrogen.

It is difficult to form any satisfactory hypothesis relative to the rational constitution of this series of acids: they may be regarded as belonging to the type of nitrous acid containing a double atom of nitrogen, and in which one atom of oxygen has been replaced by an alcohol radical, thus—



or they may be viewed as constructed upon the hyponitrous acid

type, one equivalent of oxygen being replaced by an alcohol radical, and a second atom by binoxide of nitrogen, thus—



Without attaching much value to either hypothesis, I prefer the latter.

By analogous processes, there can be little doubt that many new series of organic acids may be derived from inorganic acids, by the replacement of one or more atoms of oxygen by an alcohol-radical; in fact, my pupil Mr. HOBSON is now studying a new series containing sulphur, produced by the action of zincethyl and its homologues upon sulphurous acid: the ethyl acid of this series is formed by the replacement of one equivalent of oxygen, in three equivalents of sulphurous acid, by an alcohol-radical.

The following Table exhibits the compounds of the new series of acids, which have been described in the foregoing pages:

	Formulae.
Dinitroethylie acid	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{H}.$
Dinitroethylate of silver	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ag}.$
Dinitroethylate of copper	$2(\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Cu}) + \text{HO}.$
Dinitroethylate of zinc (crystallized)	$2(\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Zn}) + \text{HO}.$
Dinitroethylate of zinc (anhydrous)	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Zn}.$
Dinitroethylate of baryta	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ba}.$
Dinitroethylate of lime	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ca} + 3\text{HO}.$
Dinitroethylate of magnesia	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Mg}.$
Dinitroethylate of soda	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Na}.$
Double nitrate and dinitroethylate of silver	$\text{NO}_3\text{Ag} + \text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Ag}.$
Dinitroethylate of zinc and zincethyl	$\text{N}_2\text{C}_4\text{H}_5\text{O}_4\text{Zn} + \text{C}_2\text{H}_3\text{Zn}.$
<hr/>	
Dinitromethylie acid	$\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{H}.$
Dinitromethylate of zinc	$\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{Zn} + \text{HO}.$
Dinitromethylate of soda	$\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{Na} + 2\text{HO}.$
Dinitromethylate of zinc and zinemethyl	$\text{N}_2\text{C}_2\text{H}_3\text{O}_4\text{Zn} + \text{C}_2\text{H}_3\text{Zn}.$

*On some new Compounds of Silicon,**

BY F. WÖHLER AND H. BUFF.

Siliciuretted Hydrogen.—A gaseous compound of silicon and hydrogen is produced when a bar of aluminium containing silicon is connected with the *positive* pole of a Bunsen's battery of 8 to 12 cells, and made to dip into a solution of chloride of sodium. The aluminium then dissolves in the form of chloride, a consider-

* Ann. Pharm., cili, 218; civ, 94.

able quantity of gas is evolved at its surface, and many of the gas-bubbles, as they escape into the air, take fire spontaneously, burning with a white light and diffusing a white fume. When the gas is collected in a tube over water, and bubbles of oxygen passed up into it, each successive bubble produces at first a brilliant white light and a copious white fume; but this effect gradually diminishes in intensity, and at last the remaining gas will no longer burn spontaneously by contact with oxygen. This residual gas is hydrogen; the spontaneously inflammable gas, which forms but a small portion of the mixture, is siliciuretted hydrogen. When the gaseous mixture is made to escape from a glass jar provided with a stop-cock, it burns in a jet, and deposits silica round the orifice. A piece of white porcelain held in the flame, becomes stained with a brown deposit of silicon; and if the gas be made to pass through a narrow glass tube, and heated till the glass softens, a deposit of silicon is likewise obtained, and the gas which issues from the tube is no longer spontaneously inflammable. The compound has not yet been analysed quantitatively.

The formation of siliciuretted hydrogen appears to be due to a secondary action accompanying the electrolysis of the saline solution. The aluminium, forming the positive pole of the battery, combines with the chlorine and dissolves; but the quantity of aluminium removed is about one-fourth greater than that which is equivalent to the quantity of chlorine eliminated from the solution. This excess of aluminium is found to be removed in the form of alumina, uniting with oxygen derived from the water of the solution. The equivalent quantity of hydrogen is of course evolved, and part of it enters into combination with the silicon contained in the aluminium. The compound has not yet been obtained by a purely chemical reaction; but it has been observed that the hydrogen evolved when aluminium dissolves in hydrochloric acid, burns with a brighter flame than pure hydrogen, and yields a small deposit of silica.

Chloride of Silicon and Hydrogen. $\text{Si}_2\text{Cl}_3, 2\text{HCl}$.—This compound is obtained by heating crystalline silicon to a temperature somewhat below redness in a stream of hydrochloric acid gas. The silicon in fine powder is disposed throughout the entire length of a long glass tube, one end of which is connected with an apparatus for evolving dry hydrochloric acid gas, while to the other is attached a long-legged U-tube, cooled by a mixture of ice and salt, and fitted with an escape tube, having its aperture widened like a funnel, and dipping into a large vessel of ice-cold water.

As soon as the apparatus is filled with hydrochloric acid gas, the tube is surrounded with hot coals, and heated to a temperature short of visible redness; at a higher temperature, the ordinary tetrachloride of silicon would be formed. The hydrochloric acid is

then decomposed; bubbles of inflammable hydrogen gas pass through the water, and at the same time a white substance, which is a new oxide of silicon, is separated, being produced by the action of the water on a portion of the chloride of silicon and hydrogen, which is carried forward with the stream of hydrogen.

At the end of the operation, the U-tube is found to contain a turbid liquid, which is the chloride of silicon and hydrogen, mixed with other compounds. When subjected to fractional distillation it begins to boil at about 28° or 30° C, the temperature, however, quickly rising to between 40° and 43° , between which limits the largest portion of the product, which is the chloride of silicon and hydrogen, passes over. The temperature ultimately rises to 60° , and on one occasion it rose to 92° .

Chloride of silicon and hydrogen is a colourless, very mobile liquid, which has a very pungent odour, fumes strongly in the air, and covers everything around it with a white film. Its boiling point is about 42° ; specific gravity 1.65. It does not conduct electricity. Its vapour is as inflammable as ether-vapour, and burns with a faintly luminous, greenish flame, diffusing vapours of silica and hydrochloric acid. When a few drops of the liquid are passed up into oxygen gas in an eudiometer tube over mercury, and left to evaporate, a gaseous mixture is formed, which explodes violently when an electric spark is passed through it, producing a white flame and covering the inner surface of the tube with a white film of silicic acid. The residual gas consists of hydrochloric acid and terchloride of silicon, the compound having given up half its silicon to form silicic acid.

The vapour passed through a narrow red-hot tube is quickly decomposed into amorphous silicon, which coats the inside of the tube with a brown specular deposit, and a mixture of hydrochloric acid and terchloride of silicon. Hence the necessity of keeping the heat below redness during the preparation. When the vapour is passed over aluminium in the state of fusion, it is very easily decomposed, hydrogen being set free, chloride of aluminium subliming, and the remainder of the aluminium becoming covered with a loose crust of crystallized silicon. The tube is at the same time coated internally with amorphous silicon, in consequence of part of the compound being decomposed merely by the heat, in the manner above described.

In contact with water, the compound is instantly decomposed, with great rise of temperature, yielding hydrochloric acid and hydrated sesquioxide of silicon (p. 93). If a small dish full of the liquid chloride be placed over a surface of water, and the whole covered with a bell-jar, the liquid quickly disappears, and the surface of the water becomes covered with a thick crust of the oxide.

The vapour of the chloride is rapidly absorbed by alcohol and

ether, without separation of oxide. The solutions fume in the air, and when left to evaporate over sulphuric acid and hydrate of lime, they leave a partly earthy, partly translucent oxide, which appears to contain an ethyl-compound (silicic ether?). The alcoholic solution solidifies after a while into a translucent jelly.

The preceding reactions sufficiently indicate the composition of the new chloride, which is further confirmed by the analysis, giving as a mean result, 19.14 p. c. silicon and 80.98 p. c. chlorine, while the formula $\text{Si}_2\text{Cl}_3 \cdot 2\text{HCl}$ requires 19.18 Si. and 79.92 Cl.

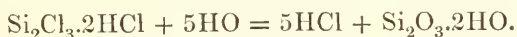
Bromide of Silicon and Hydrogen. $\text{Si}_2\text{Br}_3 \cdot 2\text{HBr}$.—Prepared like the chloride. It is at first coloured yellow by free bromine, but may be decolorised by means of mercury.

It is a colourless liquid which fumes very strongly in the air. Its specific gravity is approximately 2.5. When immersed in water, it is decomposed like the chloride, but immediately becomes covered with a coat of oxide, which for a while protects it from further decomposition.

Iodide of Silicon and Hydrogen. $\text{Si}_2\text{I}_3 \cdot 2\text{HI}$.—Prepared like the chloride and bromide, excepting that there is no necessity for a receiver, inasmuch as the iodide; being less volatile and solid at ordinary temperatures, condenses at the cool end of the tube in which the decomposition takes place.

It forms a dark red, brittle mass, which fumes strongly in the air, its colour then changing, first to bright vermilion-red, and ultimately to snow-white. It melts easily, and solidifies in the crystalline form on cooling. At a higher temperature, it boils and distils over. In the state of vapour it appears to be colourless. In water it instantly assumes a vermilion-red colour, and is slowly decomposed. Bisulphide of carbon dissolves it in larger quantity, forming a blood-red solution, which, when concentrated by distillation, deposits the compound in dark red crystals.

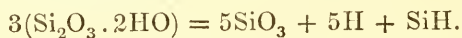
Hydrated Oxide of Silicon, $\text{Si}_2 \cdot \text{O}_3 \cdot 2\text{HO}$.—Produced in the decomposition of the preceding compounds by water: *e. g.*



It is most readily obtained as a secondary product in the preparation of the chloride (p. 92). The water must be cooled to 0°C . as the oxide is decomposed by it at ordinary temperatures. The oxide is collected on a filter, and washed with ice-cold water; the filter gradually but strongly pressed between bibulous paper; and the oxide dried over oil of vitriol.

It is a snow-white, amorphous body, very light and bulky, and floats in water, but sinks in ether. Alkalies, even ammonia, and their carbonates decomposes it, with frothy evolution of hydrogen and formation of alkaline silicates. It is not acted upon by any acid except hydrofluoric acid, which dissolves it, with rapid evolution of hydrogen. It may be heated to 300°C ., or above, without

giving off water or undergoing any other change. At a stronger heat, it takes fire, and glows brightly with a phosphorescent light, giving off hydrogen gas, which takes fire with explosion. Heated in oxygen gas, it burns with a dazzling light. It likewise burns when heated in a covered crucible, but the residual silica has more or less of a brown colour, arising from admixture of amorphous silicon, and the inner surface of the crucible becomes coated with silica. These appearances are due to the evolution and subsequent decomposition of siliciuretted hydrogen. In fact, when the compound is heated in a tube, it gives off a gas which fumes in the air, but does not take fire spontaneously, in consequence of being mixed with free hydrogen; but when set on fire it burns with separation of silica. When the hydrate is dried in a stream of hydrogen, then heated to redness, and the gas which escapes is passed through a narrow tube heated to redness at one part, the tube becomes coated with a brown speculum of silicon, and the escaping gas when set on fire yields a deposit of silicic acid on a glass plate held against the flame. If siliciuretted hydrogen has the composition SiH , the decomposition of the hydrated oxide may be represented by the equation:



Hydrated oxide of silicon is somewhat soluble in water. The acid filtrate obtained in its preparation is constantly filled with rising bubbles of hydrogen, presenting the appearance of fermentation, and the gas is evolved with such force as to project the stopper from the vessel, if closed. The decomposition may be still further accelerated by heat. The solution also gives off abundance of hydrogen when mixed with ammonia. It is a powerful reducing agent. It precipitates gold and palladium from the solutions of their chlorides, the latter, perhaps, mixed with silicate of palladium. With nitrate of silver, it first forms a white precipitate of chloride of silver, but afterwards throws down a brown substance containing silicon as well as silver. Mixed with a cupric salt and then with an alkali, it throws down yellow cuprous hydrate. With corrosive sublimate, it forms a precipitate of calomel, which, if left in contact with excess of the solution, is gradually reduced to the grey metal. From selenious, tellurous, and sulphurous acids, it precipitates respectively selenium, tellurium, and sulphur. It instantly decolorises a solution of permanganate of potash. It has no action on chromic acid, or on solutions of platinum, iridium, or indigo.

The composition of the hydrated oxide, as given by analysis, agrees nearly with the above formula. Two analyses gave in 100 parts: 50.98 and 50.99 Si; 27.34 and 27.68 O; 21.68 and 21.33 HO; the formula $\text{Si}_2\text{O}_3 \cdot 2\text{HO}$ requiring 50.35 Si, 28.37 O and 21.28 HO. In some cases, however, a larger proportion

even, 52.75 p. c. silicon was obtained, and this, together with certain reactions of the compound, leads to the supposition that there exists a lower oxide of silicon, probably SiO , and a corresponding chloride.

The lower oxide appears to be that which dissolves in water, and produces the reducing effects above mentioned; a portion of the oxide which had yielded above 52 p. c. of silicon was again mixed with water, and again washed on a filter with water at the ordinary temperature, till the wash-water exhibited with nitrate of silver, no longer a precipitate, but merely a brownish colouring. The residual oxide was found to contain only 49.05 p. c. silicon.

The chloride corresponding to the lower oxide (SiCl?) appears to be gaseous at ordinary temperatures. In one preparation, *amorphous* silicon in considerable quantity was exposed to the action of hydrochloric gas at a temperature below redness. The reaction took place with great facility, and hydrogen was abundantly evolved; but the U tube, though cooled to -15°C . was afterwards found to contain very little liquid chloride; while, on the other hand, the water through which the gas passed after leaving the U tube, contained a large quantity of white oxide, which burnt with peculiar brightness, yielding a brown coloured silica. This was the oxide which was found to contain 52.75 per cent of silica.

*Nitride of Silicon.**—This compound is obtained by the action of ammonia on either of the chlorides of silicon. It is perfectly white, amorphous, infusible, and unalterable at the highest temperatures, and does not oxidise when ignited in contact with the air. It is not acted upon by alkalies in solution, or by acids, excepting hydrofluoric acid, which converts it into silicofluoride of ammonium. When fused with hydrate of potash, it gives off a larger quantity of ammonia, and yields silicate of potash. Heated with red oxide of lead, it reduces the lead, with incandescence and formation of nitrous acid. Like nitride of boron, it eliminates carbon from carbonic acid. Fused with carbonate of potash, it yields silicate and cyanate of potash, from which urea may be prepared; if the nitride of silicon is in excess, cyanide of potassium is formed at the same time.

* H. Sainte-Claire Deville and Wöhler. *Ann. Pharm. civ.* 356.

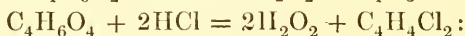
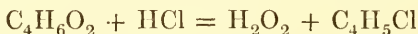
On Chloride of Ethylene.*

By A. Wurtz.

WHEN pentachloride of phosphorus is gradually added to glycol, which is kept cool, a brisk action takes place; hydrochloric acid being evolved, and the glycol being converted into a viscid mass without blackening. On adding more of the pentachloride, the mixture becomes more fluid, and after a certain time, the evolution of hydrochloric acid ceases; and any additional quantity of the pentachloride dissolves in the liquid while hot, but separates again on cooling. If the product be then distilled, it begins to boil below 100° ; but the boiling point gradually rises to above 150° , and the residue ultimately blackens. The distillate is colourless, and when redistilled, passes over completely below 115° . It contains oxychloride of phosphorus, which may be decomposed by agitation with water, and an oily liquid then separates, which, when washed with water, dried by chloride of calcium, and rectified, exhibits the properties and composition of chloride of ethylene, $C_4H_4Cl_2$. Its formation is represented by the equation:



Chloride of ethylene stands to the bi-acid compound glycol in the same relation as chloride of ethyl to the mono-acid compound alcohol.



it is the hydrochloric ether of glycol.

* Compt. Rend. xlv., 228. Ann. Ch. Pharm. clv., 174.

THE
QUARTERLY JOURNAL
OF
THE CHEMICAL SOCIETY.

VII.—*On some Compounds of Iodide and Bromide of Mercury
with the Alkaloids.*

BY THOMAS B. GROVES, F.C.S., WEYMOUTH.

I BEG leave to direct the attention of the Chemical Society to a class of compounds that I believe has not hitherto been noticed, and which I think deserves attention, as likely to afford materials whose investigation may throw additional light on that somewhat obscure but highly interesting subject, the Alkaloids.

The compounds in question are, for the most part, crystalline. Their composition is represented by the empirical formula ($\text{Hg}_2 \text{I}_3$, Alk.) and ($\text{Hg}_2 \text{Br}_3$, Alk.). ($\text{Hg} = 100$, and Alk. representing morphine, codeine, strychnine, quinine, cinchonine, &c.)

I first observed the reaction that led to this investigation on adding to a solution of iodide of mercury in iodide of potassium a small quantity of hydrochlorate of morphia. A bulky white precipitate was formed, which, when tested, revealed the presence of mercury, iodine, and morphia, and was then found to be crystallisable from alcohol and water.

Morphine, I observed, was not the only alkaloid liable to this reaction, but that all the alkaloids proper I had access to, viz.,

quinine, cinchonine, codeine, veratrine, aconitine, brucine, and strychnine, also narcotine, and a similar body I have separated from the capsule of the English poppy, and termed *diacodine*, were equally so. Salicine and aloine, however, were unaffected. The iodide of potassium and mercury may therefore be regarded as a general precipitant of the alkaloids; and seeing that these compounds are nearly, if not entirely, insoluble in cold water, and have a high atomic number, I conceive they may be advantageously applied to the determination of their atomic numbers, and also be highly useful in medico-legal investigations.

I append the individual characters of a few of the combinations containing iodine.

That of morphine is soluble to a small extent in boiling water, especially if slightly acidulated, and separates in the crystalline form on cooling. It dissolves much more readily in hot alcohol.

That of quinine is almost perfectly insoluble in boiling water, but dissolves in almost any proportion in boiling alcohol, from which the greater part again separates as a soft resinous mass on cooling. When, however, the cold solution is allowed spontaneously to evaporate, it crystallises beautifully.

That of cinchonine behaves very similarly. Its crystalline character is, however, something different, as also its solubility.

These two last are both fusible at about 200° , and when cold are very brittle, with conchoidal fracture.

That of strychnine is insoluble to any appreciable extent either in hot or cold water, and dissolves very sparingly in boiling alcohol. From this it crystallizes in a triangular form. The crystals are quite microscopic, very brilliant, and make good polariscope objects.

That of codeine is soluble in and crystallizes from hot water and alcohol, I think more freely than any that I have observed.

That of brucine is slightly soluble in water, and generally less refractory than that of strychnine; and, like it, becomes gritty soon after precipitation.

The others I need not particularise, as they have offered no details of interest.

None of them, as far as I have observed, contain water of crystallisation.

Their crystalline form is usually acicular, with, I think in most cases, a triangular section.

They are not decomposed by dilute acids, cold or hot, or by

iodide of potassium, and are only affected by *boiling* solutions of the fixed alkalies.

In obtaining them for the purpose of analysis, I have precipitated one equivalent of the alkaloid by a solution of three equivalents of iodide or bromide of potassium, and one equivalent of chloride of mercury.

I have not been able to produce a corresponding ammonia compound.

Their analysis was effected :—(1.) By dissolving a carefully dried and weighed quantity in boiling alcohol, and adding thereto an excess of recently prepared sulphide of ammonium to precipitate the mercury as HgS . The heat is kept up a few minutes to avoid the precipitation of the compound by the cooling agency of the reagent; a slight excess of nitric acid added, and the sulphide of mercury separated and weighed in the usual manner. From the filtrate deprived of sulphuretted hydrogen by the cautious application of heat, the iodine is thrown down by nitrate of silver, and the alkaloid is estimated by difference.

(2.) By precipitating, first the iodine by nitrate of silver, removing the excess of the precipitant by hydrochloric acid, and then as before.

(3.) The strychnine salt, which could not be got into convenient solution, was digested for half-an-hour with sulphide of ammonium, and then treated as before. When caustic potass is added after the sulphide, the sulphide of mercury is dissolved by the sulphide of potassium formed, and the liquid is immediately filled with crystals of strychnine fully $\frac{1}{8}$ th of an inch long.

In no case have I directly estimated the alkaloid. The concurrence of the analyses I doubtless owe to the ready and complete desiccation of the compounds.

The following are the results of analyses of the iodine compounds of morphine and strychnine which appear to justify the formula I have ascribed to them, within the limits of error :—

Analyses of the Morphine Salt.—No. 1.

	Calculation.	Analysis.
No. 1.— $\text{Hg}_2=200$	2.04	2.017
$\text{I}_3=381$	3.88	3.636
Morphia=285	2.91	3.177
<hr/>	<hr/>	<hr/>
866	8.83	8.830

	Calculation.	Analysis.
No. 2.— $Hg_2=200$	1·57	1·543
$I_3=381$	3·00	2·820
Morphia=285	2·25	2·457
<hr/>	<hr/>	<hr/>
866	6·82	6·820

Centesimal Comparison.

No. 1.	No. 2.
Mercury=22·85	=22·63
Iodine=41·18	=41·35
Morphia=35·97	=36·02
<hr/>	<hr/>
100·00	100·00

Analyses of the Strychnine Salt.

No. 1.— $Hg_2=200$	2·99	3·155
$I_3=381$	5·71	5·996
Strychnine=334	5·00	4·549
<hr/>	<hr/>	<hr/>
915	13·70	13·700

2nd Analysis of the Strychnine Salt.

	Calculation.	Analysis.
$Hg_2=200$	2·19	2·267
$I_3=281$	4·19	4·486
Strychnine=334	3·68	3·307
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915	10·06	10·060

Centesimal Comparison.

No. 1.	No. 2.
Mercury . . =23·03	=22·54
Iodine . . =43·77	=44·59
Strychnine=33·20	=32·87
<hr/>	<hr/>
100·00	100·00

On submitting, however, the compounds of quinine and cinchonia to the same treatment, I was annoyed to find a very considerable discrepancy, which I first thought was occasioned by defect of drying; but this having been proved not to have been the case, I

considered it just possible that the compound I had analysed (the amorphous mass deposited by the cooling of its alcoholic solution) had been rendered basic by the action of the solvent; that the crystals obtained from the mother liquor were possibly acid, and the *first* precipitate neutral.

Samples of each of these were carefully analysed, and the results obtained were identical.

Cinchonine was found to present the same difficulty, both yielding about as much of their respective alkaloids as would be expected were their equivalents one-fourth less than they are believed to be. Thus—

Analysis of the Quinine Salt.

	Calculation.	Analysis.
No. 1.— $\text{Hg}_2=200$	3.66	3.82
$\text{I}_3=381$	6.96	7.70
Quinine=324	5.93	5.03
<hr/>	<hr/>	<hr/>
905	16.55	16.55
No. 2.— $\text{Hg}_2=200$	1.302	1.38
$\text{I}_3=381$	2.479	2.75
Quinine=324	2.109	1.76
<hr/>	<hr/>	<hr/>
205	5.890	5.89

Centesimal Comparison.

No. 1.	No. 2.
Mercury =23.08	=23.43
Iodine. . =46.52	=46.69
Quinine =30.40	=29.88
<hr/>	<hr/>
100.00	100.00

Analyses of the Cinchonine Salt.

	Calculation.	Analysis.
No. 1.— $\text{Hg}_2=200$	3.39	3.62
$\text{I}_3=381$	6.47	7.16
Cinchonine=308	5.23	4.31
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8.89	15.09	15.09

2nd Analysis of the Cinchonine Salt.

	Calculation.	Analysis.
Hg ₂ =200	1·70	1·80
I ₃ =381	3·26	3·55
Cinchonine=308	2·64	2·25
<hr/>	<hr/>	<hr/>
889	7·60	7·60

Centesimal Comparison.

	No. 1.	No. 2.
Mercury..	=23·99	=23·69
Iodine ..	=47·45	=46·71
Cinchonine	=28·56	=29·60
<hr/>	<hr/>	<hr/>
	100·00	100·00

Taking these facts in connection with the anomalies experienced by Dr. Bird Herapath in his late experiments on his interesting discoveries, the iodo-sulphates of the cinchona alkaloids ("Pharmaceutical Journal," March, 1858), and more especially since the equivalents of Dr. Herapath approach somewhat nearly those I have referred to, I would venture to suggest whether it would not be advisable to re-open this question, by thoroughly investigating Dr. Herapath's iodo-sulphates, in connection with the double iodides.

I will here just observe in conclusion that the iodide of mercury and potassium was suggested by Dr. de Vry as a precipitant for strychnine; the knowledge that it is not *especially* so will prevent dangerous possibilities. I have also suggested the use of the compounds as internal remedies in cases where the simultaneous exhibition of mercury, iodine, and some alkaloid is indicated, and they are now undergoing a trial at the hands of several Weymouth practitioners.

VIII.—*On a new method of preparing Propionic Acid: viz. by the action of Carbonic acid upon an Ethyl compound.*

By J. A. WANKLYN, Esq.

IN the course of experiments made on the action of highly electro-positive metals upon zinc-ethyl, I obtained, some time ago, crystalline compounds containing the metal employed in union with ethyl. These bodies, of which a detailed account will shortly be published, react most energetically upon bodies containing an electro-negative constituent.

Such, indeed, is the electro-positive energy of the sodium compound, that dry carbonic acid itself is thereby decomposed, with evolution of heat, the resulting product, as will further on be proved, being propionate of soda.

I proceed to describe the experiments with carbonic acid and the new body containing ethyl and sodium.

Sodium-ethyl* was prepared by acting upon zinc-ethyl with sodium, whereby metallic zinc was precipitated and a crystalline compound containing sodium-ethyl and zinc-ethyl was produced. This body, which dissolved readily in excess of zinc-ethyl, was introduced into a bulb so constructed as to admit of the passage of a gas. On attempting to free the crystalline compound from adherent zinc-ethyl by the transmission of carbonic acid, great evolution of heat occurred, zinc-ethyl distilled off, and the contents of the bulb formed an amorphous white solid. This latter effervesced with water, forming a solution, which, when treated with sulphuric acid, evolved the odour of propionic acid. In proof that this heating and solidifying were due neither to free oxygen nor to moisture, I may mention that an experiment was made with the same apparatus, in which hydrogen was substituted for carbonic acid, and that no such effects occurred as had been noted in the former case.

Different samples of sodium-ethyl prepared from zinc-ethyl as aforesaid were exposed to the action of carbonic acid.

In one case, the subsequent treatment of the amorphous solid was as follows:—it was put into water, distilled with dilute

* Sodium-ethyl cannot be obtained by the action of sodium upon iodide of ethyl.

sulphuric acid, and the distillate subsequently redistilled alone, in order to separate anything which might have been mechanically carried over during the first distillation. The second distillate containing the dilute pure acid was warmed with carbonate of baryta, filtered and evaporated to dryness in the water-bath. The residue, which was crystalline and completely soluble in water, was afterwards dried in the air-bath at about 130°C ; until it no longer lost weight.

A baryta determination—made by moistening the salt with strong sulphuric acid, and afterwards igniting cautiously to expel the excess of sulphuric acid and the organic matter, gave this result—

·288 grm. of the substance yielded ·237 grm. of sulphate of baryta.

The substance, therefore, contained 48·38 per cent. of barium.

Propionate of baryta contains 48·41 per cent. of barium.

From another sample of sodium-ethyl, the amorphous mass given by the action of carbonic acid was treated thus:—First, with a little moist ether, whose purity had been well ascertained. The object of this deviation from the plan followed in the former case was to avoid a troublesome elevation of temperature which occurs when zinc-ethyl (adherent to the propionate of soda) is suddenly acted upon with water. After the addition of water and the expulsion of the ether which had been added, by heating in the water-bath, a distillation with dilute sulphuric acid was made as before.

The distillate, after supersaturation with carbonate of soda, was evaporated to dryness in the water-bath; and an endeavour was made to obtain concentrated propionic acid from this soda-salt by distillation with strong sulphuric acid. This operation was carefully conducted in the air-bath, the materials being contained in a small bulb retort. Neither carbonization nor evolution of sulphurous acid was observed, and the resulting distillate had the smell of propionic acid. From it a silver-salt was made by the use of pure oxide of silver. This salt, forming beautiful, but exceedingly light crystals, was crystallised by cooling its solution in hot water. The crystals were separated from the mother-liquid and dried in vacuo.

I. ·0466 grm. of the substance gave, on cautious ignition, ·0272 grm. of metallic silver.

II. A combustion was made by heating the substance placed in

a small platinum boat in a stream of dry air freed from carbonic acid. The products of combustion were led over red-hot oxide of copper, and, in fact, the arrangement was essentially the same as that which gives remarkably accurate results in the hands of Hofmann and others. So treated, .0632 grm. of the substance gave

.0447 grm. of carbonic acid.

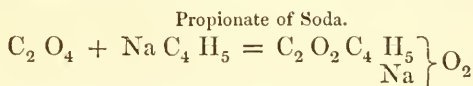
.0154 grm. of water.

.0377 grm. of silver.

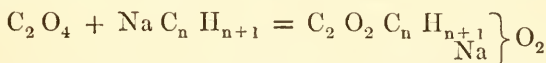
Here follow the collected results compared with the composition of propionate of silver.

Propionate of Silver.	Calculated		Found.	
			I.	II.
C ₆	36	19.89	—	19.29
H ₅	5	2.76	—	2.71
O ₄	32	17.68	—	18.35
Ag	108	59.67	58.4	59.65
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	181	100.00		100.00

The reaction which takes place between carbonic acid and sodium-ethyl admits, therefore, of the following expression:—

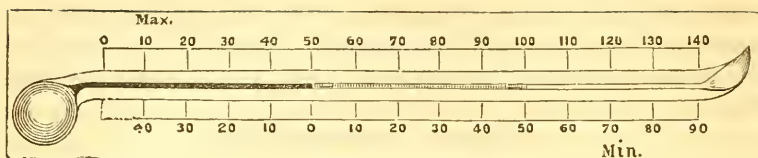


And since there can be no doubt that homologous bodies would give analogous results with carbonic acid—that, for instance, *sodium-methyl* would give acetate of soda—we may write the following as a general formula expressing the reaction which has been realized.



Inspection of the formula will at once show that a synthesis exactly corresponding to the well-known and beautiful analysis of the series of volatile fatty acids $\text{C}_2\text{O}_2 \text{C}_n\text{H}_{n+1} \left. \begin{array}{c} \\ \text{H} \end{array} \right\} \text{O}_2$ made by Kolbe some years ago, has now been effected. In fact, such a reaction as that described here is what that distinguished chemist, in conjunction with Frankland, predicted in his memoir* of last year.

* Ann. Ch. Pharm. ci. 265.



IX.—*Notice of another New Maximum and Minimum Mercurial Thermometer.*

By JOHN G. MACVICAR, D.D., Moffat.

THE maximum and minimum thermometer described by me at page 221, volume x, of this journal is not the only one in which mercury may be used to give the minimum as well as the maximum for any interval of time between two successive adjustments. A more elegant instrument, at least for meteorological purposes, may be constructed thus :—

Let a mercurial maximum thermometer of the ordinary Rutherford's construction be taken, and let 50° or 60° in length of a suitable liquid be introduced into the stem immediately above the mercury, and into this liquid let two indices be inserted, first, one which shall obey the magnet, as in Rutherford's maximum thermometer, and then one of enamel, as in Rutherford's minimum. Let the instrument be then sealed in the usual way, and on the plate let two scales be engraved, one taking its points from the top of the mercury for a scale of maximum temperatures, and the other taking its points from the top of the liquid for a scale of minimum temperatures, and the instrument is completed. To prepare for an observation, let the enamel index be brought, as in Rutherford's minimum, to the top of the liquid: then holding or placing the instrument horizontally, let the steel index be brought by the magnet to the top of the mercury. The thermometer is now fit for use. It is obvious that the upper end of the enamel index will give the minimum and the lower end of the steel index the maximum temperature since the last adjustment.

I had contrived this instrument before that described at page 221, volume x, but passed from it at the time, in apprehension of not finding a liquid suitable for the suspension of the minimum index. Spirit and analogous liquids tend to diffuse with the mer-

cury when in a horizontal column, and each breaks the continuity of the other. And though when this occurs, the instrument still remains a good mercurial minimum, yet it destroys its completeness and beauty.

I am now satisfied, however, that a liquid having no diffusive tendency or chemical action between it and mercury, as also a sufficiently low freezing point and high boiling point, may be found. In fact, between twenty and thirty years ago, Mr. Adie, the optician in Edinburgh, merely to prevent oxidation in the tubes of Rutherford's maximum thermometer, introduced above the mercury, naphtha; and I saw the other day one of these thermometers, which, during that long interval had preserved the mercurial column unbroken, and the steel index pure and all right. It is certain, however, that it is not every kind of liquid that passes in commerce under the name of naphtha that will do so. But the fact that a hydrocarbon was found which has continued to function well for a quarter of a century, shows that a suitable liquid may be found.

Residing, however, as I do, among the mountains of Scotland, far away from all facilities for accurate experiments, I must leave further determinations to those who are more favourably situated for such enquiries.

X.—*On the Atomic Weights of Oxygen and Water.**

BY WILLIAM ODLING, M.B.

SECRETARY TO THE CHEMICAL SOCIETY.

WHETHER an atom of water contains the same quantity, or double the quantity, of hydrogen that is contained in an atom of hydrochloric acid, and whether the atomic weight of oxygen is 8 or 16, are concrete examples of the many disputed questions which lie at the very basis of scientific chemistry. These many primary questions are so intimately connected with one another, that if the answer to nearly any one of them were fully agreed upon, that

* Extract from a lecture "On Atoms, Molecules, and Equivalents," delivered April 15 and May 6, 1858.

single unanimity might almost determine an entire unanimity. But to arrive at such a desirable consummation, it is necessary for some one or other of these questions to be fairly argued out upon premises that are admitted by all to be indisputable. And herein lies the great difficulty, because, in reality, each one of us has formed his opinion upon the single question, rather by its bearings upon all the other disputed questions, than from well defined premises of any kind. Each party has assumed instinctively certain points that are not proven, or are disallowed, and from these assumptions has deduced in great measure his conclusion upon all the questions. Moreover, to no one question can there be given an answer the correctness of which is proveable to demonstration. Almost every fact may be interpreted in several different ways; and it becomes an argument, from probability, from analogy, from simplicity, from consequences, as to which interpretation is most exact. But, apart from the absolute accuracy or falsity of any explanation, it is evidently most inconsequent to interpret, as many chemists do, a certain set of facts in one special manner, and a precisely similar set of facts in an opposite manner. Now, it is to this time-honoured inconsistency that I wish particularly to direct your attention.

Allow me, for a few moments, to occupy your time with such an elementary introduction to the doctrine of combination in definite proportions, as we might all agree to put before a student commencing the study of chemistry. Thus, we are acquainted with about sixty different kinds of matter which have hitherto proved undecomposable, and which we consequently term simple bodies or elements. These elements unite with one another in certain fixed or definite proportions to form an infinite variety of compound bodies. We can illustrate our meaning very well by reference to hydrogen, chlorine, and sodium; three elements that are possessed of highly characteristic properties. We find by experiment that 1 part of hydrogen unites with 35.5 parts of chlorine to form the compound body, chloride of hydrogen, or chlorhydric acid; and that 35.5 parts of chlorine unite with 23 parts of sodium to form the compound body, chloride of sodium, or common salt. We take the numbers, 1, 35.5, and 23, to represent the combining proportions of hydrogen, chlorine, and sodium respectively: and, in a similar manner, there have been assigned, to other of the elements, certain numbers which express, respectively, the least proportion of the ele-

ment that unites with 1 part of hydrogen,—or that replaces 1 part of hydrogen to unite with 35·5 parts of chlorine. Thus,

1 part of hydrogen unites with	$\left\{ \begin{array}{l} 35\cdot5 \text{ parts of chlorine,} \\ \text{or } 19 \text{ parts of fluorine,} \\ \text{or } 80 \text{ parts of bromine,} \\ \text{or } 127 \text{ parts of iodine,} \end{array} \right.$

and 1 part of hydrogen	$\left. \begin{array}{l} \text{or } 23 \text{ parts of sodium} \\ \text{or } 32\cdot5 \text{ parts of zinc} \\ \text{or } 108 \text{ parts of silver} \end{array} \right\}$	unite with 35·5 parts of chlorine.
or 23 parts of sodium		
or 32·5 parts of zinc		
or 108 parts of silver		

The proportion in which hydrogen enters into a combination, being less than that of any other element, is assumed as unity; and as the quantity of sodium, or zinc, or silver, that displaces 1 part of hydrogen from its combination with 35·5 parts of chlorine, also displaces it from its combination with 19 parts of fluorine, or with 80 parts of bromine, or with 127 parts of iodine, it is evident that the numbers 1, 19, 23, 32·5, 35·5, 80, 108, and 127, indicate generally the proportions in which the elements hydrogen, fluorine, sodium, zinc, chlorine, bromine, silver, and iodine, unite with one another. The above proportional numbers result from a common well defined relation to the standard of comparison; they are mere results of experiment uncontrolled by any theory whatever. So far as we have yet gone, our idea of the combining proportion of an element is the least quantity of the element that can unite with, or replace, 1 part of hydrogen. But this simple idea has very speedily to receive an important modification. We find the smallest quantity of nitrogen that can unite with 1 part of hydrogen, to be 4·7 parts, but the combining proportion of nitrogen is fixed, not at 4·7 parts, but at three times that quantity, or 14 parts. We find that 1 part of hydrogen unites with 35·5 parts of chlorine to form the compound chlorhydric acid, and that one part of hydrogen unites with 4·7 parts of nitrogen to form the compound ammonia. We take 35·5 as the proportional number for chlorine, why do we not take 4·7 as the proportional number for nitrogen? Why do we not express the compound body ammonia by the formula HN, precisely as we express the compound body chlorhydric acid by the formula HCl? To avoid the confusion that would arise from using the same letter to express two different quantities, we will take the symbol Az to represent 4·7 parts of nitrogen; so that

$3 \text{ HAz} = \text{H}_3\text{N}$. Now the formula HAz is in accordance with all the considerations hitherto presented to our notice, it is more simple than the formula H_3N , and, by its means, ammoniacal compounds in general might be represented as analogous to chlorine and fluorine compounds; thus,

Ammonia	HAz	HCl
Trizincamide	ZnAz	ZnCl
Trimercuramide	HgAz	HgCl
Potassamide	KAz.2HAz	KCl.2HgCl
Sal-ammoniac	HCl.3HAz	KI.3HgCl

Why then have chemists unanimously rejected the formula HAz , and adopted the formula H_3N ? Now, although this last formula may have originated in part from accident, and have been retained in part from habit, yet we have no lack of real arguments to show the necessity, or at any rate advisability, of maintaining it. I believe the principal arguments are the following:—

1°. Because it is found that a given bulk of gaseous ammonia contains three times as much hydrogen as the same bulk of chlorhydric acid.

2°. Because it is found that a given bulk of nitrogen combines with three times as much hydrogen as does the same bulk of chlorine; and that the relative weights of equal bulks of nitrogen and chlorine and hydrogen are as 14 : 35·5 : 1.

3°. Because certain undoubted analogies and ratios of nitrogenised bodies are concealed by formulæ in which $\text{Az}=4\cdot7$, and are manifested by formulæ in which $\text{N}=14$.

4°. Because, in ninety-nine cases out of a hundred, the quantity of ammonia which is the agent or resultant of a reaction must contain three units of hydrogen, or some multiple of three units of hydrogen; and consequently fourteen, or some multiple of fourteen, parts of nitrogen.

5°. Because in the majority of the compounds which ammonia forms with other bodies, the ammonia must be represented with three units, or some multiple of three units, of hydrogen.

6°. Because, although the composition of some few nitrogenised bodies may be represented most simply by formulæ, in which $\text{Az}=4\cdot7$; yet the great majority are represented most simply by formulæ in which $\text{N}=14$.

7°. Because, in ammonia, the actual or potential replacement of hydrogen takes place definitely in thirds, by three successive stages.

Although the above arguments cannot be considered to prove

absolutely to demonstration that the atom of nitrogen, or the smallest indivisible quantity of nitrogen that can enter into a combination, is really fourteen times as great as the atom of hydrogen, yet they present so great a sum of probabilities in favour of that conclusion that chemists have been unanimous in accepting it. With one exception, all these arguments apply with equal force to the elements phosphorus, arsenic, antimony, and bismuth; and we consequently find that all chemists have agreed to accept for the respective atomic weights of these bodies, three times the smallest quantity of the body which unites with 1 part of hydrogen, or with 35.5 parts of chlorine. The excepted argument is that relating to the vapour densities of the elements in question. But, in default of this argument, we can bring forward another of a most cogent nature in behalf of the triplication of the atomic weights of phosphorus, arsenic, antimony, and bismuth, namely, that derived from their gradational analogies to nitrogen. If the atomic weight of nitrogen is 14 and not 4.7, the atomic weights of phosphorus, arsenic, antimony, and bismuth must be respectively 31, 75, 120, and 213, and not the thirds of these numbers.

From the above considerations concerning nitrogen and its congeners, in which all chemists are agreed, it appears that while the determination of the smallest proportion of an element that can unite with or replace one part of hydrogen is a question purely experimental, the determination of the atomic weight of an element, or of the smallest indivisible quantity of an element that can enter into a combination, is a question for the judgment, and one that can only be decided by an intimate knowledge and due consideration of very many circumstances connected with the body. Now, although the judgment of chemists has been unanimous with respect to nitrogen and its congeners, such unanimity has not prevailed in reference to many other elements. Thus, with regard to silicon,

Thomson represented chloride of silicon by the formula,

Si Cl_2 , where the atomic weight of silicon = 7.12

Gmelin, by the formula,

Si Cl_2 , where the atomic weight of silicon = 14.25

Berzelius, by the formula,

Si Cl_3 , where the atomic weight of silicon = 21.37

Whereas, in my opinion, the balance of argument is in favour of the formula

Si Cl_4 , where the atomic weight of silicon = 28.50.

In reference to a body of such doubtful analogies as silicon, whose combinations, moreover, are remarkable for their complexity, it is fit and natural that differences of opinion with regard to its atomic weight should be entertained by different chemists, according to their particular modes of viewing the subject; and, not only with regard to silicon, but to boron, to gold, to uranium, to tantalum, and indeed to all elements the analogies of which have not been well established. But, in reference to such well known elements as oxygen, sulphur, and carbon, there certainly ought to be the same unanimity that obtains in the case of nitrogen; though in reality we find the discord even more violent than in the case of silicon.

The majority of English chemists represent the atomic weight of carbon by 6, that of oxygen by 8, and that of sulphur by 16. Dr. Frankland would double the atomic weight of carbon, but would retain the old atomic weights of oxygen and sulphur. Mr. Griffin, who lays claim to priority in doubling the atomic weights of carbon and oxygen, ridicules the notion of doubling that of sulphur. Dr. Williamson, Mr. Brodie, and myself have for a long time past advocated the doubling of all three.

Let us now proceed to investigate, from undisputed data, the atomic weight of oxygen, and of its most important compound with hydrogen, namely, water. Is the atom of water $\text{HO}=9$, or $\text{H}_2\text{O}=18$?

All chemists admit, firstly, that the atom of chlorhydric acid consists of 1 part of hydrogen united with 35·5 parts of chlorine; secondly, that the atom of ammonia consists of 3 parts of hydrogen united with 14 parts of nitrogen; and that, as compared with 35·5 parts of chlorine, 14 parts of nitrogen is the smallest quantity of nitrogen that can enter into a combination. Now I wish to show, firstly, that if the atom of chlorhydric acid consists of 1 part of hydrogen united with 35·5 parts of chlorine, and if the atom of ammonia consists of 3 parts of hydrogen united with 14 parts of nitrogen, then the atom of water must consist of 2 parts of hydrogen united with 16 parts of oxygen; secondly, that if 35·5 parts of chlorine constitute the smallest indivisible quantity of chlorine that can enter into a combination, and if 14 parts of nitrogen constitute the smallest indivisible quantity of nitrogen that can enter into a combination, then 16 parts of oxygen constitute the smallest indivisible quantity of oxygen that can enter into a combination; or, in other words, that the atomic weight of oxygen is 16, when

compared with the atomic weight of hydrogen as 1, of chlorine as 35.5, and of nitrogen as 14. Every argument that induces us to accord to the atom of nitrogen the number 14, rather than the number 4.7, should also induce us to accord to the atom of oxygen the number 16, rather than the number 8.

I propose to review briefly all the arguments we have admitted in the case of nitrogen, and to prove that they are equally applicable in the case of oxygen; or to show why it is that ammonia must be written H_3N , and water H_2O , as compared with chlorhydric acid HCl .

NITROGEN.

a. Because it is found that a given bulk of gaseous ammonia contains three times as much hydrogen as the same bulk of chlorhydric acid.

β. Because it is found that a given bulk of nitrogen combines with three times as much hydrogen as does the same bulk of chlorine; and that the relative weight of equal bulks of nitrogen and of chlorine are as 14 to 35.5.

OXYGEN.

a. Because it is found that a given bulk of gaseous water contains twice as much hydrogen as the same bulk of chlorhydric acid.

β. Because it is found that a given bulk of oxygen combines with twice as much hydrogen as does the same bulk of chlorine; and that the relative weights of equal bulks of oxygen and of chlorine are as 16 to 35.5.

I attach very great importance to these first two arguments, which apply with equal force to the duplication of oxygen and the triplication of nitrogen; to the binhydric character of water and the terhydric character of ammonia.

γ. Because certain undoubted analogies and ratios of nitrogenised bodies are concealed by formulæ in which $\text{Az}=4.7$, and are manifested by formulæ in which $\text{N}=14$.

γ. Because certain undoubted analogies and ratios of oxidised bodies are concealed by formulæ in which $\text{O}=8$, and are manifested by formulæ in which $\text{O}=16$.

These reasons apply with about equal force, though in a somewhat different manner, to nitrogen and to oxygen respectively. Thus with $\text{Az}=4.7$, the analogies of nitrogen and chlorine compounds would be concealed by the formulæ, for we should have—

Nitrous acid.

Chlorous acid.

 $\text{HAz}_3\Theta_2$ instead of $\text{HN}\Theta_2$ analagous to $\text{HCl}\Theta_2$.

Nitric acid.

Chloric acid.

 $\text{HAz}_3\Theta_3$ instead of $\text{HN}\Theta_3$ analagous to $\text{HCl}\Theta_3$.

Pernitric oxide.

Perchloric oxide.

 $\text{Az}_6\Theta_4$ instead of $\text{N}_2\Theta_4$ analagous to $\text{Cl}_2\Theta_4$.

With $\text{O}=8$, the relation of water to the alcohols as the undoubted vanishing point of the series would not be manifested, as it is in the formulæ with $\Theta=16$.

Thus, if we write alcohol $\text{C}_4\text{H}_6\text{O}_2$, wood spirit $\text{C}_2\text{H}_4\text{O}_2$, and water HO , the relation of water to the alcohols does not appear, but in the following series of formulæ it is perfectly apparent:—

$\text{C}_5\text{H}_{12}\Theta$	Amylic alcohol.
$\text{C}_4\text{H}_{10}\Theta$	Butylic „
$\text{C}_3\text{H}_8\Theta$	Propylic „
$\text{C}_2\text{H}_6\Theta$	Ethylic „
$\text{C}\text{H}_4\Theta$	Methylic „
$\text{H}_2\Theta$	Hydric „

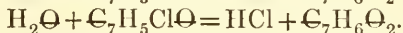
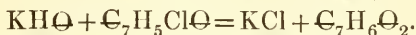
The relation of water to the alcohols, as shown in the above formulæ, is not a mere paper relation, but has its foundation in experiment. When alcohol and water respectively are acted upon by potassium, by chloride of benzoyl, by pentachloride of phosphorus, and by a host of other re-agents, the reactions are acknowledged by all to be precisely parallel. All chemists, no matter what formulæ they employ, recognise the fact that the quantity of water which, in a reaction, corresponds to one proportion of alcohol, must contain two units of hydrogen.

Similarly with regard to the hydrated bases and acids. If we write hydrate of potass KHO_2 , hydrated hypochlorous acid HClO_2 , and water HO , the relation of the formulæ as representing comparable quantities does not appear. But in the following series it is perfectly evident:—

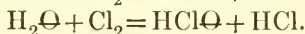
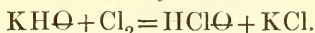
$\text{K K}\Theta$	Potass oxide.
$\text{K H}\Theta$	Potass hydrate.
$\text{H H}\Theta$	Water.
$\text{H Cl}\Theta$	Hypochlorous acid.
$\text{K Cl}\Theta$	Potass hypochlorite.
$\text{Cl Cl}\Theta$	Hypochlorous anhydride.

The following reactions, among many others, show that the quantity of water which corresponds to one proportion of hydrate of potass, or of hypochlorous acid, must contain two units of hydrogen:—

1. *Action of Chloride of Benzoyl.*



2. *Action of Chlorine.*

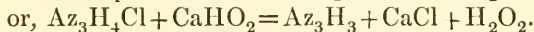


δ. Because, in ninety - nine cases out of a hundred, the quantity of ammonia which is the agent or resultant of a reaction must contain H₃, or some multiple of H₃; and consequently 14, or some multiple of 14 parts of nitrogen.

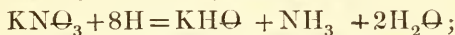
δ. Because, in ninety - nine cases out of a hundred, the quantity of water which is the agent or resultant of a reaction must contain H₂, or some multiple of H₂; and consequently 16, or some multiple of 16 parts of oxygen.

This argument is one of the most cogent that can be adduced. It is well illustrated in the case of nitrogenized, but infinitely better in the case of oxidised compounds. Let us adduce some nitrogenous reactions.

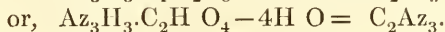
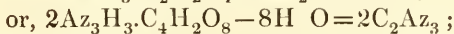
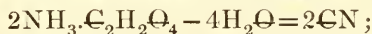
1. *Formation of Ammonia from Sal Ammoniac.*



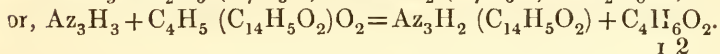
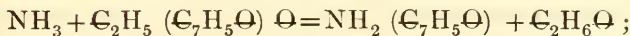
2. *Formation of Ammonia from Nitrate of Potass.*



3. *Formation of Cyanogen from Oxalate of Ammonia.*

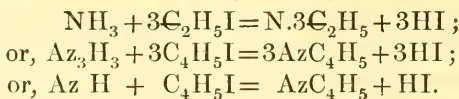


4. *Formation of Benzamide.*



Express the above reactions howsoever you please, you cannot represent any one of them with a proportion of ammonia containing less than 3 units of hydrogen, nor consequently with less than 14 parts of nitrogen. And, whenever more than 3 units of hydrogen are required, you must take some multiple of three units of hydrogen, and some multiple of 14 parts of nitrogen; and ninety-nine cases out of a hundred will yield the same result. As an example of those cases in which it is possible to represent the acting or resulting proportion of ammonia with less than three units of hydrogen, I may adduce the—

5. *Formation of Triethylamine.*

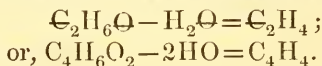


And similarly with trimercuramine, $\text{NHg}_3 = 3 \text{ AzHg}$; though no one really thinks of writing the formulæ of these bodies with only one unit of ethyl or of mercury respectively.

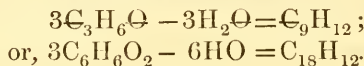
Let us now revert to oxygenous reactions. I wish to show that, in ninety-nine cases out of a hundred, where water appears as the agent or resultant of a reaction, it is impossible to represent that water with less than two atoms of hydrogen.

1°. Whenever an alcohol, ketone, or other oxidised organic compound yields a hydrocarbon by dehydration, the water eliminated contains two, or some multiple of two, units of hydrogen.

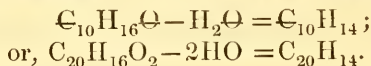
1. *Formation of Olefiant Gas from Alcohol.*



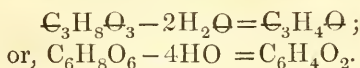
2. *Formation of Mesitylene from Acetone.*



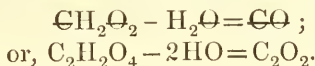
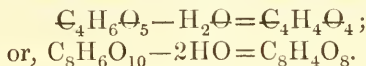
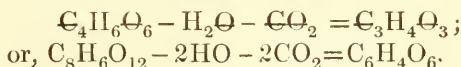
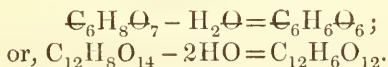
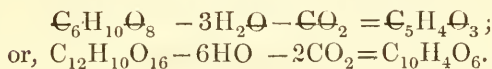
3. *Formation of Cymene from Camphor.*



Other compounds than hydrocarbons result from similar equations, thus—

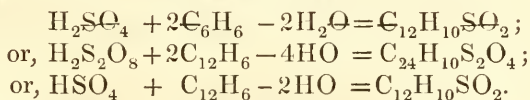
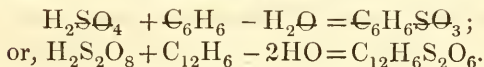
4. *Formation of Acrolein from Glycerin.*


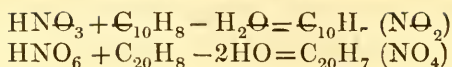
2° Whenever an organic acid yields a pyroacid, or other pyrogenous product, by dehydration :—

 1. *Formation of Carbonic Oxide from Formic Acid.*

 2. *Formation of Maleic, from Malic Acid.*

 3. *Formation of Pyruvic, from Tartaric Acid.*

 4. *Formation of Aconitic, from Citric Acid.*

 5. *Formation of Pyromucic, from Mucic Acid.*


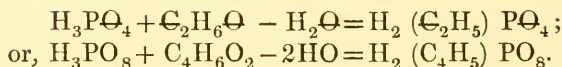
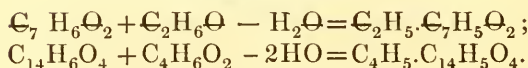
3°. Whenever two compounds act upon one another to form a new compound, with simultaneous elimination of water.

Action of an Acid upon a Hydrocarbon.

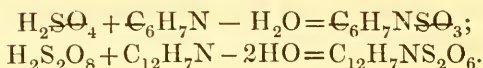
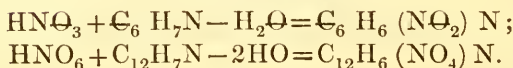
 1. *Sulphobenzide.*

 2. *Sulphobenzidic Acid.*


3. *Nitro-naphthaline.*

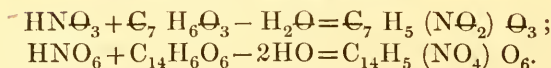
Action of an Acid upon an Alcohol.

4. *Phosphovinic Acid.*5. *Benzoic Ether.*

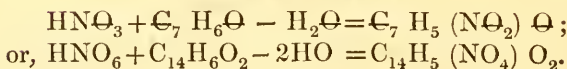
Action of an Acid upon an Alkali.

6. *Sulph-anilic Acid.*7. *Nitraniline.*

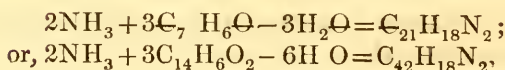
Action of an Acid upon an Acid.

8. *Nitrosalicylic Acid.*

Action of an Acid upon an Aldehyd.

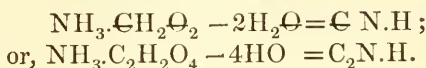
9. *Nitro-benzoic Aldehyd.*

Action of an Alkali upon an Aldehyd.

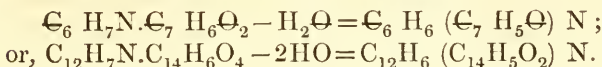
10. *Hydrobenzamide.*

4°. Whenever a salt of ammonia, aniline, or other volatile alkali loses water.

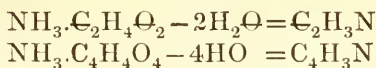
1. *Formation of Cyanhydric Acid.*



2. *Formation of Benzanilide.*



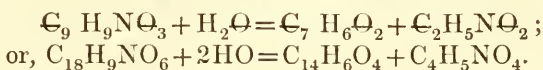
3. *Formation of Aceto-nitrile.*



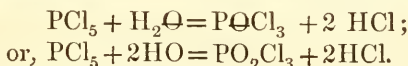
In all the illustrations hitherto brought forward, the water has been the resultant of the reaction. Many of these reactions are capable of being reversed, and the water then appears as the agent of the reaction.

But we can also adduce an abundance of other and most varied instances in which water is the agent of a reaction.

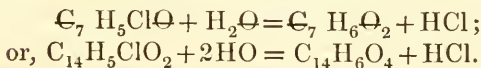
1. *Decomposition of Hippuric Acid.*



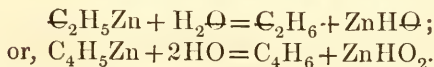
2. *Decomposition of Pentachloride of Phosphorus.*



3. *Decomposition of Chloride of Benzoyl.*



4. *Decomposition of Zinc-ethyl.*



The circumstance that 2HO are invariably associated, is strongly suggestive of their being inseparably associated, of their constituting in fact but one atom.

ε. Because, in the majority of the compounds which ammonia forms with other bodies, the ammonia must be represented with three units, or some multiple of three units, of hydrogen.

ε. Because, in the majority of the compounds which water forms with other bodies, the water must be represented with two units, or some multiple of two units, of hydrogen.

We may take aldehyd-ammonia $\text{C}_2\text{H}_4\text{O}_2.\text{NH}_3$, and ammoniacal sulphate of zinc, $\text{Zn}_2\text{SO}_4.4\text{NH}_3$, as nitrogenous illustrations. The oxygenous illustrations are innumerable, including nearly all cases of water of crystallization. We may take as examples:—

{ Fructose	..	$\text{C}_6\text{H}_{12}\text{O}_6$;	or, $\text{C}_{12}\text{H}_{12}\text{O}_{12}$.
{ Glucose	..	$\text{C}_6\text{H}_{12}\text{O}_6.\text{H}_2\text{O}$;	or, $\text{C}_{12}\text{H}_{12}\text{O}_{12}.2\text{HO}$.

{ Dextrine	..	$\text{C}_6\text{H}_{10}\text{O}_5$	or, $\text{C}_{12}\text{H}_{10}\text{O}_{10}$.
{ Lactine	..	$\text{C}_6\text{H}_{10}\text{O}_5.\text{H}_2\text{O}$;	or, $\text{C}_{12}\text{H}_{10}\text{O}_{10}.2\text{HO}$.

Hydrate of turpentine	$\text{C}_{10}\text{H}_{16}.3\text{H}_2\text{O}$;	or, $\text{C}_{20}\text{H}_{16}.6\text{HO}$.
Hydrate of alloxan	$\text{C}_4\text{H}_2\text{N}_2\text{O}_4.\text{H}_2\text{O}$;	or, $\text{C}_8\text{H}_2\text{N}_2\text{O}_8.2\text{HO}$.

ζ. Because, although the formulæ of some few nitrogenized bodies may be represented most simply by formulæ in which $\text{Az}=4.7$, yet the great majority are represented most simply by formulæ in which $\text{N}=14$.

ζ. Because, although the formulæ of some few oxidized bodies may be represented most simply by formulæ in which $\text{O}=8$, yet the great majority are represented most simply by formulæ in which $\text{O}=16$.

This argument applies strongly in the case of nitrogenized, but much more strongly in the case of oxydized compounds.

Ammonia, and all derivatives of ammonia in which the whole of the hydrogen is replaced by one single kind of metal, or hydrocarbon, or haloid, might be represented more simply by formulæ in which $\text{Az}=4.7$, than by formulæ in which $\text{N}=14$. Thus triethylamine is written most simply $\text{Az}\text{C}_2\text{H}_5$, though most correctly by $\text{N}3\text{C}_2\text{H}_5$.

I believe that all other nitrogenized bodies are necessarily represented most simply by formulæ in which $\text{N}=14$.

With regard to oxygen, all hydrated oxides, double oxides, hydrated acids, oxy-salts, aldehyds, ketones, alcohols, pseudo-saline ethers, and various other descriptions of compounds, doubt-

less forming together 99 per cent. of all known compounds of oxygen, cannot be represented so simply by formulæ in which $O=8$ as by formulæ in which $\Theta=16$.

I have contended that if the comparable atoms of nitrogenized bodies were correctly formulated, they would all of them be represented more simply by formulæ in which $N=14$, than by formulæ in which $Az=4\cdot7$; and I now contend that if the comparable atoms of oxidized bodies were correctly formulated, they would all be represented more simply by formulæ in which $\Theta=16$, than by formulæ in which $O=8$. But precisely as there are some few nitrogenized bodies which, with the symbol $Az=4\cdot7$, may be divided into thirds, and can thus receive simpler formulæ than with the symbol $N=14$, so are there some comparatively few oxidized bodies which, with the symbol $O=8$, may be divided into halves, and can thus receive simpler formulæ than with the symbol $\Theta=16$. These bodies are the following:—

1°. Most compounds in which oxygen is united with one kind of matter only, including nearly all the simple metallic oxides.

Thus with $\Theta=16$, water and lime must be written respectively $H_2\Theta$ and $Ca_2\Theta$, analogous to hydrate of lime $CaH\Theta$; but with $O=8$ they may be written thus— H_2O_2 and Ca_2O_2 , analogous to hydrate of lime $CaHO_2$; or thus— HO and CaO . I do not propose to argue the point whether CaO , or $Ca_2O_2 (=Ca_2\Theta)$, is the correct expression for a metallic oxide, lime; any more than I have argued the point whether $HgAz$, or $Hg_3Az_3 (=Hg_3N)$, is the correct expression for a metallic nitride, mereuramine. We are at present discussing whether the formula of water is HO or $H_2O_2 (=H_2\Theta)$, and the decision upon this point will determine that of the metallic and other simple oxides. It may be observed, however, that many strictly comparable reactions can be effected by means of lime, hydrate of lime, and water respectively, and that in these cases we always require $2HO$, or $2CaO$, to effect the reaction. Of course, if Ca_2O_2 is the correct expression for the atom of lime, the formula with $\Theta=16$ is simpler than that with $O=8$, and similarly with other homogeneous oxides.

2°. Bodies analogous to ordinary ether and the homogeneous anhydrides. With $\Theta=16$, ether and benzoic anhydride must be written respectively—

$Et_2\Theta$	analogous to	$H\ Et\ \Theta$	and	$Me\ Et\ \Theta$
Ether.		Alcohol		Methyl-ethyl-ether;

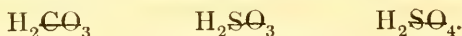
and $\text{Bz}_2\Theta$ analogous to $\text{H Bz } \Theta$ and $\text{Ot Bz } \Theta$
Benz-anhydride. Benzoic acid Othyl-benz-anhydride;

but with $\text{O}=8$ they may be written thus:—

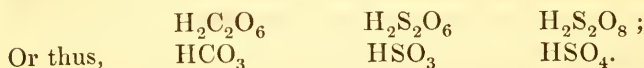
$\text{Et}_2 \text{O}_2$ analogous to H Et O_2 and Me Et O_2 ;
and $\text{Bz}_2 \text{O}_2$ analogous to H Bz O_2 and Ot Bz O_2 ;
or thus:— Et O and Bz O .

Now all arguments, founded on mode of formation, on reactions, on vapour-densities, on seriated position and properties, &c., tend to show that EtO and BzO are not correct expressions of the nature of the bodies represented;* and if Et_2O_2 and Bz_2O_2 are the correct expressions, it is at once evident that in these cases formulæ with $\Theta=16$ are simpler than formulæ with $\text{O}=8$.

3°. Certain acids, and their salts of one metal, heretofore usually considered monobasic, but which in reality are bibasic. Thus with $\Theta=16$ the hydrated carbonic, sulphurous, and sulphuric acids must be represented respectively by the formulæ:—



But with $\text{O}=8$ they may be represented thus,



But, in these cases, we can adduce strong evidence to show that the simple formulæ HCO_3 , HSO_3 , and HSO_4 , are not correct expressions of the nature of the bodies; and if the correct expressions are $\text{H}_2\text{C}_2\text{O}_6$, $\text{H}_2\text{S}_2\text{O}_6$, and $\text{H}_2\text{S}_2\text{O}_8$, that is to say, if the acids are bibasic, then the formulæ with $\Theta=16$ are evidently more simple than those with $\text{O}=8$. We shall presently advert to the distinctions between monobasic and bibasic acids.

* I mean to say that ether, by its mode of formation and chemical reactions, by its vapour density and other physical properties, belongs to the following series of strictly comparable substances, and that its formula is not $\text{C}_4\text{H}_5\text{O}$, but $\text{C}_8\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_{10}\Theta$, *vide* Williamson, Journal of Chemical Society, vol. iv.

Vinic Ethers.

$\text{H O. C}_4\text{H}_5\text{O}$	$\text{H. C}_2\text{H}_5\Theta$	Hydro-ethylic.
$\text{C}_2\text{H}_3 \text{O. C}_4\text{H}_5\text{O}$	$\text{C}_2\text{H}_3. \text{C}_2\text{H}_5\Theta$	Methyl-ethylic.
$\text{C}_4\text{H}_5 \text{O. C}_4\text{H}_5\text{O}$	$\text{C}_2\text{H}_5. \text{C}_2\text{H}_5\Theta$	Ethyl-ethylic.
$\text{C}_6\text{H}_7 \text{O. C}_4\text{H}_5\text{O}$	$\text{C}_3\text{H}_7. \text{C}_2\text{H}_5\Theta$	Propyl-ethylic.
$\text{C}_8\text{H}_9 \text{O. C}_4\text{H}_5\text{O}$	$\text{C}_4\text{H}_9. \text{C}_2\text{H}_5\Theta$	Butyl-ethylic.
$\text{C}_{10}\text{H}_{11} \text{O. C}_4\text{H}_5\text{O}$	$\text{C}_5\text{H}_{11}. \text{C}_2\text{H}_5\Theta$	Amyl-ethylic.

η Because, in ammonia, the actual or potential replacement of hydrogen takes place definitely in thirds, by three successive stages.

η Because, in water, the actual or potential replacement of hydrogen takes place definitely in halves, by two successive stages.

We have no definite nitride that can be represented as ammonia in which one-half the hydrogen is replaced, as we might expect if the atomic weight of nitrogen were 4.7. We have no definite oxide that can be represented as water, in which one-third the hydrogen is replaced, as we might expect if the atomic weight of oxygen were 8. Thus,

Chloride.	Oxide.	Nitride.
KCl	KO	HAz
KCl.HgCl	KO.HO	Wanting
KCl.2HgCl	Wanting	HAz.2PtAz

If we write water $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$, and ammonia $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$, we at once see the

necessity or reason for the vacancies. In water we can replace a half, but not a third. In ammonia we can replace one-third or

two-thirds, but not a half; whereas in marsh gas $\left. \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{C}$, we can

replace one-fourth, two-fourths, or three-fourths, but not one-third, or two-thirds of the hydrogen. We are acquainted with many ammonias in which 1, 2, and 3 thirds of the hydrogen are replaced, such, for instance, as

NH ₂ K	Potassamide
NHI ₂	Biniodamide
NHg ₃	Trimercuramine

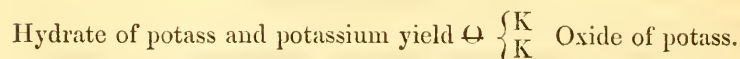
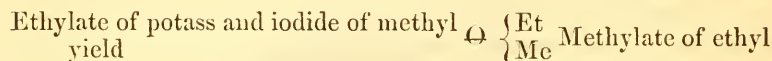
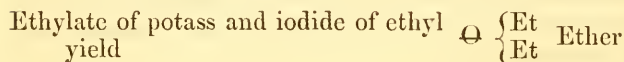
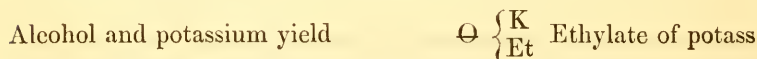
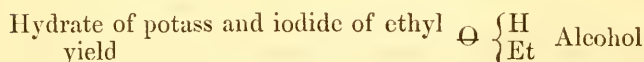
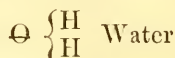
But the most striking illustration of replacement by thirds is afforded by Hofmann's researches on the volatile alkaloids, in which he successively replaced 1, 2, and 3 atoms of hydrogen by a mere continuation of one and the same process.

Ammonia.	Ethylia.	Diethylia.	Triethylia.	Ethyl-methyl-aniline.
N $\left\{ \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix} \right.$	N $\left\{ \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{Et} \end{smallmatrix} \right.$	N $\left\{ \begin{smallmatrix} \text{H} \\ \text{Et} \\ \text{Et} \end{smallmatrix} \right.$	N $\left\{ \begin{smallmatrix} \text{Et} \\ \text{Et} \\ \text{Et} \end{smallmatrix} \right.$	N $\left\{ \begin{smallmatrix} \text{Ph} \\ \text{Et} \\ \text{Me} \end{smallmatrix} \right.$

We are acquainted with many oxides that may be considered as derivatives of water, in which one half the hydrogen is replaced, or in which both halves are replaced by different elements or groupings. Thus,

Water.	Alcohol.	Ether.	Methyl-ether.	Phenyl-ether.	Ethylate of potass.
$\ominus \begin{Bmatrix} \text{H} \\ \text{H} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{H} \\ \text{Et} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Et} \\ \text{Et} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Et} \\ \text{Me} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Et} \\ \text{Ph} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Et} \\ \text{K} \end{Bmatrix}$
Hydrate of potass.	Oxide of potass.	Zinc oxide of potass.	Hypochlorite of potass.	Hypochlorous acid.	Hypochlorous anhydride.
$\ominus \begin{Bmatrix} \text{H} \\ \text{K} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{K} \\ \text{K} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Zn} \\ \text{K} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{K} \\ \text{Cl} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{H} \\ \text{Cl} \end{Bmatrix}$	$\ominus \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$

In many cases we can effect the total replacement by the same element or grouping at two successive stages. Thus,



This brings to a conclusion my arguments upon the atomic weights of oxygen and water, founded on a comparison of the arguments which apply in the case of nitrogen and ammonia. The point that I urge is not so much the absolute point, namely, that the atomic weight of oxygen must be 16, as the relative point, namely, that if the atomic weight of nitrogen is 14 and not 4.7,

the atomic weight of oxygen must be 16 and not 8. Every argument that applies to the first case, applies with equal, if not greater force, to the second. I know very well that some of the arguments I have adduced, as that from analogy, for instance, may be apparently subverted by the subterfuge of writing water H_2O_2 ; but I also know that chemists who make use of the formula H_2O_2 to represent water, act most inconsistently, if they do not also make use of the formulæ H_3Az_3 to represent ammonia. There are three consequent methods of formulating chlorhydric acid, water, and ammonia in respect to one another, namely,

I.	II.	III.
HCl	HCl	HCl
HO	H_2O_2	H_2O
HAz	H_3Az_3	H_3N

The first method was that employed by Dalton, who wrote ammonia $\text{O}\oplus=1+5$, and water $\text{O}\odot=1+7$.

But both the following modes are most inconsequent, and therefore reprehensible:—

IV.	V.
$\text{HCl} = 2 \text{ vol.}$	$\text{HCl} = 2 \text{ vol.}$
$\text{HO} = 1 \text{ vol.}$	$\text{H}_2\text{O}_2 = 2 \text{ vol.}$
$\text{H}_3\text{N} = 2 \text{ vol.}$	$\text{H}_3\text{N} = 2 \text{ vol.}$

Series IV. represents irrelative quantities, and series V. accords irrelative formulæ to comparable quantities. I would observe, in reference to series I., II., and III., that the selection of one or other of them involves both a question of fact and a question of convenience. Whether the first or the second series really represents comparable quantities, that is to say, whether the atom of water, or the smallest proportion of water that is the agent or resultant of a reaction, contains twice as much hydrogen as the atom, or smallest reacting and resulting proportion of hydrochloric acid, is a question of fact. Whether the formula in the second, or that in the third series is the most appropriate mode of expressing the fact, may be, to some extent, at least, a question of convenience, though at the same time it is one of very considerable importance. The same remarks apply to the formulæ for ammonia.

But we have an additional argument in favour of the duplication of the atom of oxygen, derived from the series into which it

enters. Thus in all compounds of oxygen with two other kinds of matter, as particularly instanced by ox-acids and oxy-salts, the oxygen increases by 16 parts; and in none of these compounds can we add, subtract, or replace a less quantity than 16 parts of oxygen. Why this should be, unless the 16 parts constitute an indivisible proportion, or chemical atom, I am at a loss to conceive. The following are illustrations :—

Chlor-hydric acid	HCl	or HCl
Hypochlorous acid	HClO	or HClO ₂
Chlorous acid	HClO ₂	or HClO ₄
Chloric acid	HClO ₃	or HClO ₆
Perchloric acid	HClO ₄	or HClO ₈
Phosphuretted hydrogen	H ₃ P	or H ₃ P
Chlorophosphoric aldehyd	Cl ₃ P $\overline{\text{O}}$	or Cl ₃ PO ₂
Hypophosphorous acid	H ₃ P $\overline{\text{O}}$ ₂	or H ₃ PO ₄
Phosphorous acid	H ₃ P $\overline{\text{O}}$ ₃	or H ₃ PO ₆
Phosphoric acid	H ₃ P $\overline{\text{O}}$ ₄	or H ₃ PO ₈
Ethylene	H ₄ C ₂	or H ₄ C ₄
Aldehyd	H ₄ C ₂ $\overline{\text{O}}$	or H ₄ C ₄ O ₂
Acetic acid	H ₄ C ₂ $\overline{\text{O}}$ ₂	or H ₄ C ₄ O ₄
Glycolic acid	H ₄ C ₂ $\overline{\text{O}}$ ₃	or H ₄ C ₄ O ₆
Chloride of carbon	Cl ₂ C	or Cl ₂ C ₂
Phosgene	Cl ₂ C $\overline{\text{O}}$	or Cl ₂ C ₂ O ₂
Formic acid	H ₂ C $\overline{\text{O}}$ ₂	or H ₂ C ₂ O ₄
Carbonic acid (hydrated)	H ₂ C $\overline{\text{O}}$ ₃	or H ₂ C ₂ O ₆

Precisely as the triplication of nitrogen necessarily leads to the triplication of phosphorus and its congeners, so must the duplication of oxygen lead to the duplication of sulphur and its congeners. Every argument that applies to the duplication of oxygen applies with almost equal force to the duplication of sulphur, even that argument derived from the combining volume of sulphur vapour, provided the researches of Bineau are trustworthy. One important consequence arises from the duplication of the atomic weight of sulphur, namely, the necessary representation of the sulphurous and sulphuric acids as bibasic. Now the question of basity is a purely experimental one. If we find the sulphurous

and sulphuric acids to have the properties of bibasic acids, we have a strong corroboration of the high atomic weights of sulphur and oxygen. But if we should find the sulphurous and sulphuric acids to have the properties of monobasic acids, that single circumstance would be of itself almost sufficient to discredit the view which accords to oxygen the atomic weight 16, and to sulphur the atomic weight 32.

I.

Certain oxacids have the following properties:—

a. Each of them can form *but one* kind of ether. This is neutral in its properties. Within two volumes of its vapour there is contained *but one* volume of ethyl or alcohol residue.

β. Each of them can form a chloride, or rather chloraldehyd, within two volumes of the vapour of which is contained *but one* volume of chlorine. Each chloraldehyd can exchange chlorine for peroxide of hydrogen to reform the normal acid, but *there is not* any compound intermediate between the chloraldehyd and the normal acid.

γ. Each of them, by reacting with ammonia, can form *but one* primary amide. This is neutral in its properties.

δ. They *cannot* any of them form stable well-defined acid salts, or salts with two or more metallic bases.

ε. They *cannot* any of them form

II.

Certain other oxacids have the following properties:—

a. Each of them can form *two* ethers, the one neutral, the other acid; for example, sulphatic ether and sulpho-vinic acid. Within two volumes of the neutral ether there are contained *two* volumes of alcohol residue.

β. Each of them can form a chloraldehyd, within two volumes of the vapour of which are contained *two* volumes of chlorine. These chloraldehyds can each exchange chlorine for peroxide of hydrogen to reform the normal acid; but *there is* a compound intermediate between the chloraldehyd and the normal acid, so that the conversion may be effected at two successive stages. Thus chloro-sulphuric aldehyd can produce first, chlorhydro-sulphuric acid, and then, normal sulphuric acid.

γ. Each of them, by reacting with ammonia, can form *two* primary amides, the one neutral, the other acid; for example, sulphamide and sulphamic acid.

δ. Each of them *can form* stable, well-defined acid salts, exactly intermediate in composition between the neutral salt and the free acid, such for instance as the bisulphate of potass. Each of them *can form* well defined double salts, in which either one-half or one-fourth the basic hydrogen is replaced by a basylous metal, the quantity of reacting acid, however, being twice as great in the second case as in the first. Common alum is an example of the second variety, potass-sulphate of nickel an example of the first. The acids of this class, moreover, produce various ill defined hybrid salts, in which the basic hydrogen of the acid is replaced by an indefinite number of metals in indefinite proportions.

ε. Each of them *can form* double

double or multiple ethers, that is, ethers with two or more varieties of alcohol residue.

ζ. They *cannot* any of them form double or multiple amides, that is, amides with two or more varieties of ammoniacal residue.

η. They *cannot* any of them form etheramides, or compounds containing both alcoholic and ammoniacal residues.

θ. They *cannot* any of them form complex acids by reacting with hydrocarbons.

ι. As a general rule, the acids of this class are more volatile than those of the succeeding classes, while their salts are more soluble. They very rarely yield anhydrides by direct dehydration, or form anhydro-salts. They do not form distinct varieties of salts, such as have received the prefixes para-, meta-, iso-, &c. Acids which have the properties described under the above heads are classed as *monobasic* acids.

κ. It is observable that when a monobasic acid reacts upon another monobasic acid to form a new acid by the elimination of water, the new acid has also the properties of a *monobasic* acid; for example, nitro-benzoic acid.

ethers, that is, ethers with two varieties of alcohol residue in equal proportions; for example the double sulphate of ethyl and methyl, the double carbonate of ethyl and amyl, &c.

ζ. Each of them *can form* double amides, that is, amides with two varieties of ammoniacal residue in equal proportions; for example, anilo-sulphamide, or anilo-carbamide.

η. Each of them *can form* double etheramides, that is, compounds with an alcoholic and an ammoniacal residue in equal proportions; for example, sulphi-methane, or sulphamethylane.

θ. Each of them *can form* complex acids by reacting with hydrocarbons; for example, the sulpho-benzidic and sulph-ethylenic acids.

ι. As a general rule, the acids of this class are less volatile than those of the preceding class, while their salts are less soluble. They yield anhydrides by direct dehydration; they form anhydro-salts, and also distinct varieties of salts, such as have received the prefixes para-, meta-, iso-, &c. Acids which have the properties described under the above heads are classed as *bibasic* acids.

κ. It is observable, that when a bibasic acid reacts upon a monobasic acid to form a new acid by the elimination of water, the new acid has also the properties of a *bibasic* acid; for example, sulpho-benzoic acid.

There are many other distinctions between the two classes of acids, but the above are the most important. Sulphurous and sulphuric acids therefore are considered to be bibasic, simply because they are possessed of certain properties which are characteristic of bibasic acids, without any reference whatever to their formulæ. The circumstance of their bibasity, as far as it goes, is in favour of the duplication of the atoms of sulphur and oxygen, from which such bibasity follows as a necessary consequence, inasmuch as with these high atomic weights it is impossible to represent the acids as being other than bibasic. With $O=8$ and $S=16$, the formulæ for the bibasic acids would be $H_2S_2O_6$ and $H_2S_2O_8$ respectively, than which the formulæ H_2SO_3 and H_2SO_4 are evidently more simple. Moreover, we are thus enabled to formulate two natural series of acids.

Chloric	HClO_3	HClO_4	Perchloric
Sulphurous	H_2SO_3	H_2SO_4	Sulphuric
Phosphorous	H_3PO_3	H_3PO_4	Phosphoric

The properties of tribasic, and quadribasic, are as well defined as are those of bibasic acids. Thus a tribasic acid can form three ethers, two of them acid and one neutral. Also, a chloraldehyd which, within two volumes of vapour, contains three volumes of chlorine. Also, three amides, two of them acid and one neutral. Also, acid and double and treble salts, in which the hydrogen and bases are related to one another by thirds. Also, treble ethers, treble amides, treble etheramides, &c., &c. In reference also to the basity of sulphuric acid, I might start from another point, and show, by parallel arguments, that for every property of phosphoric acid which causes it to be recognized as tribasic, there is a similar property of sulphuric acid which must cause it to be considered as bibasic, precisely as I have shown that the accordance of a terhydric character to ammonia necessitates the accordance of bi-hydric character to water.

With regard to the duplication of carbon, it is found that carbonic and sulpho-carbonic salts have bibasic properties, and must consequently be written HMC_2O_6 , $\text{M}_2\text{C}_2\text{O}_6$, $\text{M}_2\text{C}_2\text{S}_6$, &c. Also, that the smallest quantities of carbonic oxide, carbonic anhydride, and sulpho-carbonic anhydride, that are the agents or resultants of reactions, contain twice the quantity of substance usually represented by their respective formulæ; or, in other words, that their real formulæ are C_2O_2 , C_2O_4 , and C_2S_4 . By making these few alterations, all compounds of carbon become formulated with an even number of carbon-atoms, so that nothing is easier than to substitute one large carbon atom, C having the value 12, for two small carbon atoms, C_2 having each the value 6. In this way, the anomaly of the increment of carbon, in homologous series, always taking place by two inseparable atoms is done away with, as is also the anomaly of the atomic heat of carbon.

XI.—*On the General Characters of the Iodo-Sulphates of the Cinchona-Alkaloids.*

By W. BIRD HERAPATH, M.D., F.R.S.E.

IN a paper recently presented to the Royal Society, entitled "Researches on the Cinchona Alkaloids," the author has had the honour of communicating the discovery of a class of salts, analogous to the sulphate of iodo-quinine, first described in the *Phil. Mag.*, March, 1852, and the crystallography of which was subsequently more fully elicited in a paper which appeared in the *Proceedings of the Royal Society*, vol. vi.

The optical and chemical characters of these remarkable new bodies present many points of striking similarity; yet a careful examination will disclose differences, more especially in their optical properties, sufficient to induce the author to propose the formation of these optical salts as a means of recognizing each of the cinchona alkaloids, or as a method of ascertaining their purity, for which and for a complete description of these beautiful compounds, the author begs to refer to his original paper, or to the abstract of the 2nd part, read at the Royal Society, Nov. 26 ultimo.

In the present communication, only a brief abstract of the principal optical properties will be given, so as to enable each salt to be recognised, and the general chemical characters of the class will be enumerated; but the main object of the present paper is the communication of the details of the author's analytical results obtained in his investigations; from which he has been led to infer that these alkaloids, during their formation, experience some remarkable change, not analogous to substitution, however, but more allied to a splitting up of the constituent molecules and re-arrangement of these amongst themselves. This, however, is a matter still open for confirmation, and requires further research from other experimentalists.

They all contain sulphuric acid, iodine and an organic base, more or less modified in character.

They are very soluble in boiling alcohol sp.gr. 837, and crystallize on cooling with striking physical characters, by which they can be readily distinguished optically.

1st. The quinine salt is characterised by its brilliant can-

tharidin-green reflected tint and strong tourmaline powers of absorption on light; the transmitted light is polarised in one principal plane, and when analyzed by any medium, as a Nicol's prism or tourmaline, or by two similar plates superposed, when the axes are parallel, appears nearly colourless, having merely a slightly pale greenish tint, but when polarised perpendicularly to the axes, exhibits a position of maximum polarisation and absorption, marked by a reddish light or body colour. The salt is characterised crystallographically, by being derived from a right rhombic prism, obtuse angles 115° and acute 65° , having planes of truncation parallel with and perpendicular to the long axis, by which prisms are produced, α and β , which exhibit appearances of maximum absorption when the planes of their length are at right angles to a plane polarised beam as in the α prism, or parallel with the plane polarised beam as in the case of the β prism.*

2nd. The quinidine salt is known by crystallizing in long quadrilateral prisms, possessing a deep garnet red colour, with a purplish superficial reflection tint, and having a very slight double absorption or tourmaline power, the body colour being a dark brownish red.

3rd. The cinchonidine optical salt, by having equal tourmaline powers with the quinine salt; being also derived from a rhombic prism, but with angles of 137° and 43° . It presents its maximum degree of absorption, when the long axes of the primary rhomboid lie in a plane parallel with that of the polarised beam, therefore vertically, if examined by light polarised by reflection; in this case, it agrees with the quinine salt. If these plates are very thin, the transmitted tint or body colour is violet blue or indigo-coloured; but thicker plates wholly absorb light. The tint transmitted when the plates of polarisation are parallel is slightly coloured only, pale olive-green as in quinine when very thin, but yellowish green if thicker plates are examined. The reflected tint is golden or brassy yellow; and is a beam polarised in a plane parallel with that reflected from glass; it is exhibited when a plane bisecting the long axis of the primary rhombic crystal is in a plane parallel with that of the incident light, and also of reflection. The truncation planes are the same as in the quinine salt, and produce α and β prisms.

This salt, when observed in mass in contact with fluids or glass, exhibits a green tint compounded from the blue body colour, and the brassy yellow reflected rays.

* *Vide* Proceedings of Royal Society, vol. vi., *et sequent.*

4th. The cinchonidine of Wittstein differs from that of Pasteur in producing an iodo-sulphate, having a deep yellow or sienna brown transmitted light, and an olive brown or dull reddish brown reflected tint. This salt is strongly doubly absorptive, like quinine and cinchonidine; but its body colour is sienna brown or deep bistre. The quantity did not admit of analysis.

5th. The cinchonidine of Pasteur forms two other iodo-sulphates, one characterised as long silky golden aciculæ, possessed of slighter optical powers, which on dissolving in boiling spirit crystallizes as the optical salt (No. 3); and a dry dark olive-green residue; this is derived by drying the silky salt over sulphuric acid at 62° or on exposure to 212° . This also, by being re-dissolved in spirit, crystallised as the optical salt, whilst the optical crystals are reconverted into the silky by repose in an acid spirituous solution.

6th. The cinchonine salt is characterised by its long acicular form, deep purplish red colour by transmission, and dark purple blue reflection tint, like iodine. Thin plates transmit a lemon yellow; the transmitted light is polarised in one plane principally; the body colour is deep sienna or bistre brown according to thickness.*

Chemically, these salts are all more or less soluble in spirit, giving a deep sherry-brown solution, from which water precipitates them in an amorphous form as dark brown, cinnamon brown, or purplish brown precipitates. They are only very slightly soluble in dilute spirit, and scarcely at all in water or ether, turpentine or chloroform.

Acetic, diluted sulphuric, or hydrochloric acid has but little action upon them; whilst hydrochloric or sulphuric acid concentrated decomposes them.

Nitric acid rapidly acts on them even cold—with violent evolution of nitrous acid and production of heat—iodine being liberated in a crystalline form.

Alkalies decompose them also.

Sulphuretted hydrogen, soluble sulphides, sulphurous acid and sulphites, together with chlorine water, instantly discolour their alcoholic solution, with production of hydriodic acid.

In dilute alcoholic solutions, starch gives immediate evidence of iodine.

Nitrate of silver gives a yellowish white precipitate of iodide of silver and some organic basic compound, which can only be

* *Vide* Proceedings of Royal Society for further description of the optical properties.

removed by the action of concentrated nitric acid; this reaction is accompanied by the disengagement of nitrous acid vapours, with vehemence; but it requires boiling to wholly decompose the compound.

Baryta salts exhibit the existence of sulphuric acid, which in all instances is an essential constituent in their formation.

The Quinine Salt.—The analyses formerly published of this salt being defective in many respects, and incomplete from the absence of any combustion or estimation of carbon, hydrogen and nitrogen, it has long been in contemplation by the author to re-examine this subject. Circumstances having lately greatly increased the necessity of doing so, in consequence of the discovery of other salts belonging to the same class; but one more especially, viz.: the cinchonidine salt, so closely similar to it that considerable probability existed of the former substance having been impure.*

To avoid a similar inconvenience, it was first necessary to produce some perfectly pure di-sulphate of quinine. For this purpose the purest commercial di-sulphate was selected by the ether test; and the last traces of cinchonidine and quinidine were removed by first preparing the mixed alkaloids; dissolving in ether, evaporating nearly to dryness, dissolving in alcohol, and slow spontaneous evaporation. As no crystals separated under either of these processes, the salt was again converted into di-sulphate, and re-crystallized from very large quantities of distilled water. Two ounces of the di-sulphate were originally employed, and as these were re-crystallized from two quantities of three pints of boiling distilled water, and a third time from one and a half pint, it is presumable that all the extraneous sulphates were entirely removed, more especially as the non-crystallization from the ethereal and alcoholic solutions showed no evidence of their previous existence in any quantity.

In the former process employed by the author,† a mixture of acetic acid and alcohol was employed to dissolve the di-sulphate of quinine, and convert it into the neutral salt, which is alone necessary for the production of these crystals. It was thought desirable to omit the acetic acid in the present instance and employ diluted sulphuric acid, which attained the same end, and at the same time prevented the loss of half the quinine as acetate which occurred before, and at the same time got rid of

* Phil. Mag., Sept. 1852.

† Phil. Mag., Sept. 1852.

all idea of acetic acid or its elements entering into the composition of the crystals.

(a). I took 60 grains of the purified di-sulphate; dissolved it in one ounce of water acidulated with 14 drops of pure sulphuric acid 1.845 sp. gr.; assisted its solution by heat; when fully dissolved added four ounces of water and nine ounces rectified spirit; raised the temperature to 130° Fah.; and then added 40 grains of iodine previously dissolved in four ounces of hot rectified spirit. The mixture having been well agitated, was set in repose to crystallize. After twelve hours repose, the crystals were separated on a filter, and well washed with cold dilute spirit ($\frac{1}{3}$ spt.), until they no longer presented an acid re-action; the crystals were then dried by expression between folds of bibulous paper.

This mass was dissolved in 20 ounces of rectified spirit .837 by boiling and filtered rapidly; on cooling and repose, the salt again separated. The crystals were collected on a filter, washed with cold spirit, dried by expression as before, and again re-dissolved in 20 ounces of spirit, to which a little tincture of iodine was added, in order to correct the last trace of sulphate of quinine and facilitate the washing; then set in repose, separated on a filter, washed with cold, dilute and weak spirit; then with water; dried by expression and exposure to the air; and then further dried in a hot water oven at 200° Fah. after being finely powdered; it was thus exposed five hours; about 64 grains were obtained.

β and γ . A second and third quantity were prepared by similar processes.

The plan followed by the author in all the analyses was the following:—

a. Iodine.—The salt was dissolved in alcohol by boiling, and nitrate of silver added whilst hot; time given for subsidence; the clear fluid decanted and passed through a filter; the residue in the beaker treated with concentrated nitric acid as before described; the resulting iodide collected on the same filter, well washed, dried and fused, the ashes of the filter being deducted as usual. To the filtered acid solution, pure chloride of sodium was added, and the resulting chloride of silver removed by filtration, &c.

β . To this, chloride of barium was added in excess, and time given for the sulphate to deposit, which was collected with great care, washed, dried, and ignited. Some of the analyses were made with nitrate of baryta, which accounts for the slight excess.

γ. The combustions were all most carefully made with chromate of lead, and copper employed to arrest any iodine. The potass bulbs had an extra bulb, &c. attached, containing fused potass, and the last portions of carbonic acid were swept out of the combustion tube by a current of dry and pure oxygen gas, which was retained in a gasometer and passed through a U-tube filled with potassa and chloride of calcium, the stream being perfectly under control by carefully regulating the pressure, and by a stop-cock interposed.

δ. The water of crystallization was obtained in some instances only, by the method previously used,* viz:

By mixing weighed portions of the dry salt with pure iron reduced in hydrogen gas, and by exposing the mixture in an oil bath at 400° Fah. to a current of dry hydrogen, the water being caught in a counter-poised chloride of calcium tube.

ε. The nitrogen was determined by M. Peligot's process—

An acid was employed having a sp. g. of 1·01494 at 60° Fah.
510 gr. measures of which gave 24·91 grs. sulphate of baryta
= 8·516 sulphuric acid dry.

Now 200 measures were always carefully employed, with every precaution against loss, and exactly saturated by 1000 gr. measures of a standard soda-solution.

The 200 measures = 3·338 sulphuric acid = 1·1683 nitrogen.

The ammonia = X acid measures—these are all given in the results, the formula being 200 : 1·1683 :: X : N.

Having prepared some perfectly pure optical iodo-sulphate of quinine, it was dried very carefully at 62°, then exposed over sulphuric acid during many days, until it ceased to lose weight, then submitted to Liebig's drying bath during four hours; 29·68 grs. lost ·74 grs. water = 2·49 per cent. water.

Dry residue gave the following results:—

- | | | | |
|---|-------------------------------|------|---|
| { | a | I. | 20·26 of the dry residue gave |
| | | | iodide of silver 11·32 grs. |
| | | | sulphate of baryta 6·02 grs. |
| | | II. | 6·01 grs. gave iodide of silver 3·35 grs. |
| | | | „ sulphate of baryta 1·63. |
| | | III. | 8·25 grs. burnt with chromate of lead and oxygen gas, |
| | gave carbonic acid 12·57 grs. | | |
| | „ water 3·54 grs. | | |

* Phil. Mag. 1852.

β	IV. 11.43 grs. burnt with soda-lime gave iodide of silver 6.45 grs.
	V. 14.37 grs. gave iodide of silver 8.43 grs. „ sulphate of baryta 4.05 grs.
	VI. 8.15 grs. gave iodide of silver 4.78 grs. „ sulphate of baryta 2.33 grs.
	VII. 6.65 grs. burnt with chromate of lead and oxygen. gave carbonic acid 10.080 grs. „ water 2.85 grs.
	VIII. 10.33 grs. gave carbonic acid 15.71 grs. „ water 4.225 grs.
γ	IX. 9.445 grs. gave by Peligot's process for nitrogen, ammonia = 60° gr. M. acid (200° = 1.1683 N.) = .35049 N.
	X. 8.432 grs. gave by Peligot's process, ammonia = 48 acid measures (200 = 1.1683 N.) = .285592 nitrogen
	XI. 9.78 grs. gave, burnt with chromate of lead, &c. carbonic acid 14.72 grs. water 4.17 grs.

Quinine-salt, analyses leading to the following centesimal results:—

	α			β					γ			Mean.
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
Iodine .	30.195	30.033	—	30.50	31.729	31.69	—	—	—	—	—	30.8295
Sul. Acid	10.246	9.352	—	—	9.631	9.854	—	—	—	—	—	9.7705
Carbon .	—	—	41.554	—	—	—	41.34	41.456	—	—	41.048	41.3496
Hydrogen	—	—	4.766	—	—	—	4.762	4.544	—	—	4.737	4.7025
Nitrogen	—	—	—	—	—	—	—	—	3.711	3.38	—	3.5455
Oxygen .	—	—	—	—	—	—	—	—	—	—	—	9.8024
												100.0000
		III				VII	VIII			XI		
Carbonic Acid .		152.3636				151.58	152.004			150.511		151.614
Water		42.911				42.857	40.90			42.638		42.326

and they produce the following ratio:—

Iodine24275 =	2.	atoms.
Sulphuric acid24426 =	2.012	„
Carbon	6.8582 =	56.546	„
Hydrogen	4.7025 =	38.74	„
Nitrogen2532 =	2.086	„
Water at 212°2764 =	2.27	„

and lead to the following composition:—

		Theory.	Expt. Means.
57 Carbon	. 342 =	41·606 = CO ² 152·55	41·3496
38 Hydrogen	38 =	4·623 = HO 41·607	4·7025
2 Nitrogen	. 28 =	3·409	3·5455
10 Oxygen	. 80 =	9·730	9·8024
2 Iodine	. 254 =	30·900	30·8295
2 Sulp. acid	80 =	9·732	9·7705
		<hr/>	<hr/>
		822 100·000	100·000

which, with two 2 atoms of water additional, constitutes the optical salt dried over sulphuric acid at 60° Fah.

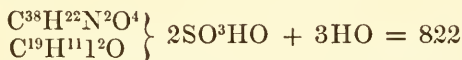
1 dry residue as above	822 =	97·857
2 water	18 =	2·143
		<hr/>	<hr/>
		840	100·000

possibly arranged thus



which appear to show that the alkaloid does not enter into its constitution as quinine; but that it receives an affix, during the production of the salt, of carbon and hydrogen and oxygen, the amount of which can only be known upon determining the true composition of quinine. If, with Laurent, we assign to quinine the formula $C^{38}H^{22}N^2O^4$, we require $C^{19}H^{16}O^6$ to be added, together with 2 iodine and 2 sulphuric acid, in order to constitute the dry residue, and 2 atoms more water to produce the green optical crystals.

Thus quinine



which with 2 atoms of water constitute the beautiful optical salt already described by the author



which would give the following results

Modified alkaloid	52·738
Iodine	30·900
Sulphuric acid	9·732
7 Water	6·75
		<hr/>
		100·000

These results differ somewhat from those previously published by the author; but may be easily accounted for by the discovery of an iodo-compound so remarkably similar as the iodo-sulphate of cinchonidine proves to be, which contains more iodine.

The purity of the substance formerly analysed is therefore very problematical — especially as in the production of that salt, the author merely selected the purest commercial di-sulphate, and employed it without submitting it to any preliminary purification.

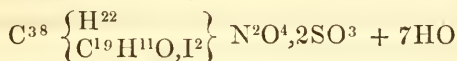
In the former communication, abundant evidence of a change in constitution was elicited by the examination of the optical properties of the restored alkaloid, and at that time the author was disposed to refer these appearances to molecular re-arrangement of the base, whereby it became analogous to the γ -quinine, having lost 2 atoms of basic HO—thus becoming a monohydrate of the organic radical $C^{20}H^{12}NO^2$ of which α -quinine was considered the tri-hydrate, quinidine (β -quinine) the bi-hydrate, and γ -quinine the mono-hydrate, by Van Heiningen.* These speculations of the author's must, however, give way to the result obtained in the foregoing analyses, which have been made with great care, and in a much more perfect manner than before, and upon substances as pure as could be obtained, made at different times and yielding very concordant results. He therefore ventures to hope, that the present idea of its constitution will eventually prove correct in the hands of other experimentalists; he is the more confident in this matter as the above theoretical constitution receives additional support from his examinations of the three salts of cinchonidine, which appear to be parallel and homologous salts. But in what manner these affices are obtained, the author cannot presume to say in the present state of the question, but ventures to suppose that during the production of the salt, a splitting of an atom of alkaloid occurs, the group $C^{19}H^{11}O$ passing over to the quinine, &c. to form the optical salt, and the $C^{19}H^{11}N^2O^3$ existing in the solution in some other state of combination, water being also assimilated. This view is not discordant with the idea gaining ground in the chemical world, that the organic alkaloids are nitrile bases in which in quinine, &c., the $C^{38}H^{22}O^4$, are representatives of 3 atoms of hydrogen.

If we decide with Gerhardt, however, that quinine contains

* Scheik, Onderzoek v, 319, and Pharmac. Centralblatt 1850, p. 90,

$C^{40}H^{24}N^2O^4$, it follows that the affix contains C^2H^2 less than that previously assigned to it herein.

On these assumptions we have two different formulæ for the optical salt. With Laurent,



and with Liebig and Gerhardt,



Both formulæ containing the same numbers of each different element and leading to the same atomic weight and centesimal results, and derived from the splitting of 1 atom quinine and the assimilation of 7 water, 5 of which are simply water of crystallisation, and 2 are inherent to the sulphuric acid.

The recent investigations of Strecker would appear to fix the atom of quinine as that given by Gerhardt,* &c.

It is quite evident on inspection that ethyl or any of its compounds cannot enter into the constitution of this salt; we must, therefore, assume the derivation of the group from the splitting of the alkaloid itself into its constituent groups, and the re-arrangement of these groups amongst themselves without any substitution of hydrogen or formation of hydriodic acid.

The further study of this interesting class of salts seems pregnant with important matter, bearing on the real constitution of the natural alkaloids in question.

SULPHATE OF IODO-QUINIDINE.

Process for manufacture in quantity.—240 grs. of quinidine of Pasteur† were dissolved in 1 ounce of diluted sulphuric acid containing 1-9th part of acid, 1·845, the solution being assisted by heat; the liquid was then mixed with 10 fluid ounces spt. ·837, and 20 fluid ounces of distilled water, the temperature raised to 130° Fah., and then 13·5 grains of iodine dissolved in 1 ounce of spt. ·837, gradually added, stirring well after each addition; on cooling, a mass of acicular crystals was produced; these were removed by filtration, and the operation was successively repeated a dozen times; by these means a large crop of crystals was at length obtained, all perfectly uniform in optical characters. They were first purified by well washing with diluted spirit, then with distilled water, and recrystallized repeatedly from rectified spirit;

* *Vide* Quart. Journal of Chemical Society, 1856.

† The quinidine of Leers is the cinchonidine of Pasteur.

on the third recrystallization, they were considered sufficiently pure for analysis. Water must not be employed in washing the crystals after recrystallization, cold spirit only should be employed. If too much iodine be used at each attempt at production, an amorphous and resinoid mass is obtained mixed with the crystals, from which it is difficult to purify them.

The alcoholic mother-liquids from these recrystallizations, furnish a further crop of similar crystals on diluting with equal quantities of boiling distilled water and setting in repose. On drying these crystals whole, they decrepitate on again exposing them to atmospheric air.

The solubility of the iodo-sulphate of quinidine was determined, thus:

65.79 grs. were boiled in 2250 gr. measures of alcohol, having sp. g. .837 at 62° Fah., in a retort; the condensed spirit returned from time to time, then filtered rapidly, whilst hot, on a counterpoised filter, which was washed with a little cold spirit, dried at 212° and weighed = 4.525 grs. remained.

∴ 2250 grs. alcohol, at 180° (omitting expansion by boiling), dissolved 61.265 ∴ $2250 \times .837$

$$\frac{\quad}{61.265} = 30.73$$

Consequently, 1 grain of this salt requires nearly 31 parts by weight of alcohol (.837), at 180° to dissolve it.

The greater portion recrystallized on cooling :

1000 grs. by measure of the alcoholic solution, at 62° Fah., were treated with nitrate of silver, and the precipitated iodide boiled in nitric acid until all reaction ceased; the iodide, washed and fused, weighed 5.4 grs.

A second experiment gave 4.78 grs.; mean 5.09 = iodine 2.750; which at 39.874 per cent. = 6.897 grs. salt.

and $1000 \times .837$

$$\frac{\quad}{6.897} = 121 \text{ grs. to dissolve 1 gr.}$$

The deep marone or garnet red coloured crystals had, at 62° Fah., sp. gr. 1.7647.

Analyses of the Sulphate of Iodo-Quinidine.

Salt dried at 212° Fah., during six hours :—

I. 14.52 grs. gave iodide of silver 10.633 = 73.23 per cent.

„ sulphate of baryta 2.7023 = 18.611.

- II. 15.82 grs., gave iodide of silver 11.63 = 73.54.
 „ sulphate of baryta 2.915 = 18.426
- III. 20.12 grs., gave iodide of silver 14.85 = 73.80.
- IV. 11.55 grs., gave sulphate of baryta 2.12 = 18.355.
- V. 7.32 grs., burnt with chromate of lead, gave—
 carbonic acid—
 water 2.62 grs. = 35.695 per cent.
- VI. 8.35 grs., burnt with chromate of lead and oxygen, gave—
 carbonic acid 10.07 = 120.598.
 water 2.975 = 35.629.
- VII. 12.66 grs., burnt in the same manner, gave—
 carbonic acid 15.14 = 119.59.
 water 4.59 = 36.256.
- VIII. 9.53 grs., burnt as before, gave—
 carbonic acid 11.457 = 120.22 grs.
 water 3.418 = 35.865.
- IX. 11.32 grs., gave with iron and hydrogen, in oil bath at 400° Faht.—
 water .803 = 7.092 water, per cent.
- X. 15.61 grs., also dried at 212°, gave, with iron and hydrogen, in oil bath at 400° Faht.—
 water 1.145 = 7.334 water, per cent.
- XI. 4.91 grs., burnt with soda-lime, by M. Peligot's process, for nitrogen (acid sp. g. 1.01493 at 60° Faht., 200° = N 1.1683) = 37.4 gr. measures, SO³HO = ammonia = N .21847 = 4.44 per cent. N.

The above results of the analysis of the quinidine salt lead to the following centesimal computations—

	Herapath.									Muspratt.			
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	I.	II.	III.	IV.
Iodine . . .	39.57	39.74	39.88	—	—	—	—	—	—	39.73	39.831	—	—
Sulphuric acid	6.39	6.326	—	6.302	—	—	—	—	—	—	6.263	—	—
Carbon . . .	—	—	—	—	—	32.89	32.615	32.787	—	—	—	31.998	32.311
Hydrogen . .	—	—	—	—	3.966	3.953	4.028	3.985	—	—	—	4.001	3.937
Nitrogen . .	—	—	—	—	—	—	—	—	4.44	—	—	—	—
Oxygen													

The author, having supplied Dr. Sheridan Muspratt with a quantity of this salt, has been most obligingly furnished with the results of his examination; from which it will be seen that those previously obtained by the author have been confirmed in the most satisfactory manner by that experienced analyst.

The subjoined is an abstract of his results :—

After three hours' exposure to 212° in a hot water bath, with a current of dry air, it suffers no further loss at the same temperature, after seven hours' additional exposure to the bath.

Two determinations of iodine gave—

I. Iodine	39.73	
II. „	39.831	Mean 39.780
Sulphuric acid 6.263 per cent.		

Two combustions of this salt dried at 212° for seven hours, gave—

III. Carbon	31.998	Hydrogen	4.001
IV. „	32.311	„	3.937
Herapath.		Muspratt.	
Mean of 3 determinations of—			
Carbonic acid	120.136		117.8995
4 Water .	35.861		35.721

These results give the following ratio :—

Carbon .	5.4606	=	34.91
Hydrogen .	3.9245	=	25.1
Nitrogen .	3.170	=	2.027
Iodine .	3.128	=	2.
Sulphuric acid .	1.5597	=	1.

		Theory.	Experiment.	Means of Muspratt.
35 Carbon .	210 =	32.9670	32.764	32.154
25 Hydrogen .	25 =	3.9244	3.984	3.969
2 Nitrogen .	28 =	4.3956	4.440	—
10 Oxygen .	80 =	12.5592	12.743	—
2 Iodine .	254 =	39.8744	39.730	39.780
1 Sulphuric acid .	40 =	6.2794	6.339	6.263
		637	100.0000	100.000

and would require—

Carbonic acid .	120.879
Water .	35.321

and probably produce the following formula—



The formula herein given, does not accord with the constitution of quinidine as given by Gerhardt.

It requires the addition of C^5H^5 to the organic base, to produce $C^{40}H^{24}N^2O^4$.

The process for producing the Cinchonidine optical salt is the following.—The alkaloid should be dissolved in a slight excess of diluted sulphuric acid—as shewn by litmus paper; to this should be added about 15 times the bulk of rectified spirit, and warmed to 100° Faht., then tincture of iodine should be added in considerable quantity, continuing the agitation after each addition. On cooling, golden sparkling crystals are deposited in radiating bunches, if suffered to remain in repose. These crystals have a golden greenish appearance in contact with glass and fluid, and are different to a practised eye from the deep blue green of quinine salt.

The cinchonidine employed must give no reaction of quinine or quinidine, with chlorine and ammonia, and must be wholly soluble in warm ether, crystallizing on cooling, in hard shining rhombic prisms.

The following proportions answer admirably:—

120 grains of pure alkaloid were dissolved in half a fluid ounce of diluted sulphuric acid (1 to 9), to this was added 10 fluid ounces of rectified spirit, and raised to 100° Faht.; with these were then mixed 48 grains iodine, dissolved in $3\frac{1}{2}$ fluid ounces of warm spirit, the whole having been well agitated, it was placed in repose; after 8 hours, a beautiful crop of golden sparkling greenish crystals were deposited; these were very thin, and presented the beautiful blue body colour so indicative of this salt.

On treating the mother-liquid after filtration, with a second quantity of iodine as before, another crop of crystals formed on cooling. These were collected on the same filter, pressed dry, then expressed on bibulous paper as strongly as possible.

The whole was then boiled in sufficient spirit to redissolve it, and again crystallized on cooling; again filtered, and now well washed with dilute spirit (1 to 3) until free from acid reaction. A second and third time was this operation performed, in these latter adding a little tincture of iodine to ensure conversion of all the sulphate into the crystals, and facilitate the washing, which was at length completed by cold distilled water. The mass dried at 212°, weighed 53·7 grains, but the alcoholic liquid still con-

tained a considerable quantity in solution, as nearly one pint of spirit was employed at each recrystallization, in order that the salt should be obtained as pure as possible.

The acid alcoholic mother-liquid, on repose, gave a large crop of golden-yellow, silky, acicular crystals, in long radiating prisms very like to asbestos, and of a golden colour; these are almost opaque to transmitted light, but when broad enough, transmit a yellow colour; they are very slender, delicate, and excessively bulky.

This salt was removed by filtration, washed with dilute cold spirit until free from all acid reaction, and pressed dry in bibulous paper; then again broken up in dilute spirit and well agitated, filtered, washed, and again pressed and dried by exposure to air until it cease to lose weight.

For analysis, this must be spread out in thin films on a counterpoised capsule, over sulphuric acid, taking the weight from time to time, then subsequently exposing it to the drying apparatus. It cannot be recrystallized except in an acid solution; in alcohol, it forms the optical salt after redissolving.

The dry olive-coloured residue also becomes the optical salt after re-solution.

Several of the analyses of the optical salt were made from such converted specimens, due care being taken to purify them as before.

The substances analysed in the accompanying schedule were made at different times, and as described, obtained by various methods.

Analyses of the Sulphate of Iodo-Cinchonidine.

Purified as described, dried in a hot bath, at 212° , during 4 hours, until the weight remained constant.

- I. 17.17 grs., gave iodide of silver $12.63 = 73.511$ per cent.
- „ sulphate of baryta $4.19 = 24.461$ per cent.
- II. 18.34 grs., gave iodide of silver
- „ sulphate of baryta $4.63 = 25.26$.
- III. 16.35 grs., gave iodide of silver $11.92 = 73.021$.
- „ sulphate of baryta $4.23 = 25.871$.
- IV. 14.37 grs., gave sulphate of baryta $3.7075 = 25.80$.
- V. 11.18 grs., gave iodide of silver $8.12 = 72.62$.
- „ sulphate of baryta $2.88 = 25.352$.
- VI. 10.906 grs., gave carbonic acid $13.97 = 128.1$.

- VII. 6.17 grs., gave carbonic acid 8.09 = 131.118.
 „ water 2.40 = 38.894.
- VIII. 5.73 grs., gave carbonic acid 7.52 = 131.239.
 „ water 2.22 = 38.708.
- IX. 8.33 grs., gave with iron and hydrogen, at 430 Fah.
 4 hours.
 water .65 = 7.803 per cent.
- X. 8.535 grs., gave water as before .68 = 7.967.
- XI. 11.36 grs., gave iodide of silver 8.12 = 71.479.
 „ sulphate of baryta 2.88 grs. = 8.593 SO³.
- XII. 5.30 grs., burnt with soda-lime, by M. Peligot's process,
 ammonia = 27° m. acid (200° acid, sp. g. SO⁴HO =
 1.1493 at 60° = 1.1683 N) 27° = N.15782 = 2.976
 per cent.

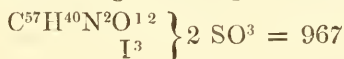
These results lead to the percentage computations for the cinchonidine optical salt—

	A							B			
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	XI.	XII.	Mean.
Iodine . . .	39.727	39.462	—	39.246	—	—	—	38.488	—	—	39.478
Sulphuric acid	8.39	8.673	8.882	8.858	8.704	—	—	8.593	—	—	8.701
Carbon . . .	—	—	—	—	—	34.936	35.73	35.792	—	—	35.486
Hydrogen . . .	—	—	—	—	—	—	4.321	4.301	—	—	4.311
Nitrogen . . .	—	—	—	—	—	—	—	—	—	2.976	2.976
Oxygen . . .	—	—	—	—	—	—	—	—	—	—	9.038

and produce the following ratio—

Iodine . . .	3.111 or atoms	3
Sulphuric acid . . .	2.175	2.097
Carbon . . .	59.14	57.013
Hydrogen . . .	43.112	41.57
Nitrogen . . .	2.12	2.045

which produce the following formula provisionally—



	Theory.	Experiment.
57 Carbon . . . = 342 =	35.367	35.486
40 Hydrogen . . . = 40 =	4.147	4.3112
2 Nitrogen . . . = 28 =	2.884	2.976
12 Oxygen . . . = 96 =	10.052	9.0388
3 Iodine . . . = 381 =	39.297	39.478
2 Sulphuric acid = 80 =	8.294	8.701
	<hr/> 967	<hr/> 100.000

and would give—	Theory.	Experiment.
Carbonic acid	129·68	130·152
Water	37·323	38·708



The author has rejected the determinations of the water of crystallization in this salt by means of iron and hydrogen gas, as only approximative, as quinoline distils at the same time, and unless the temperature be well regulated, the water appears very considerably increased in amount from this cause; some experiments have given as much as 32·22 per cent.

The yellow silky salt of cinchonidine may be produced without the optical salt at one operation.

Thus, 60 grains of cinchonidine were dissolved in half a fluid ounce of diluted acid containing 35·00 grains of dry acid; on solution, 5 ounces of spirit '837, were added, and the whole was raised to 80° Fah., to these were introduced 47·5 grains of iodine dissolved in 3½ ounces of spirit. After 12 hours' repose, the beaker was filled with a dense fibrous mass of the yellow silky salt, with only a few optical crystals sparingly disseminated; after 3 days' further repose, these were wholly converted into the silky salt. They were separated by filtration, and purified by washing and expression as before described; when thoroughly free from acid, they were dried on a porous brick, and after some days' exposure to the air, properly protected, were placed over sulphuric acid in a counterpoised vessel.

From the formula employed, it is easily found that the acid was 1·04 per cent. in the original fluid, out of which nearly half the acid was necessary to combine with the cinchonidine, as acid sulphate ($\text{C}^{38}\text{H}^{22}\text{N}^2\text{O}^2 + 2\text{SO}^3\text{HO}$). This would, at first sight, lead us to imagine that the salt may contain double the quantity of acid. But the analysis of the dry residue obtained by heating the salt in Liebig's apparatus does not warrant such a conclusion, whilst water alone is lost during this operation. Moreover, the behaviour of these three substances with alcohol proves that the acid, iodine, and base, are in the same relative proportions.

Analyses of the dry olive-coloured residue, dried during six hours in Liebig's apparatus.

* This formula requires 6·132 per cent. water.

- I. 5.03 grs. gave iodide of silver 3.77 grs. = 74.95 per cent.
 „ sulphate of baryta 1.345 grs. = 26.74 per cent.
 II. 7.91 grs. gave iodide of silver 5.915 grs = 74.77 per cent.
 „ sulphate of baryta 1.91 grs. = 24.14 per cent.
 III. 4.505 grs. gave carbonic acid 5.96 grs. = 132.30.
 „ water 1.64 grs. = 36.404.
 IV. 4.92 grs. gave carbonic acid 6.44 grs. = 130.8943.
 „ water 1.785 grs. = 36.28.
 V. 6.557 grs. gave by Peligot's process
 Ammonia = 32 grs. measures acid = .18696 N
 (200° = 1.1683 N) = 2.851 per cent. nitrogen.
 VI. 9.43 grs. gave, when burnt with chromate of lead,
 „ water 3.45 grs. = 36.585.

CINCHONIDINE.

These analyses give the following composition for the dry olive-coloured residue :

	I.	II.	III.	IV.	V.	VI.	Mean.
Iodine	40.504	40.407	—	—	—	—	40.455
Sulphuric acid	9.064	8.324	—	—	—	—	8.699
Carbon	—	—	36.082	35.689	—	—	35.8855
Hydrogen	—	—	4.045	4.031	4.065	—	4.0470
Nitrogen	—	—	—	—	—	2.851	2.851
Oxygen	—	—	—	—	—	—	8.0625

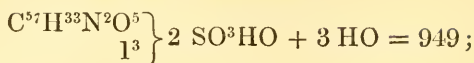
giving the following ratio :

Iodine	.318	=	3 atoms
SO ³	.2174	=	2.050
Carbon	5.9809	=	56.42
Hydrogen	4.0470	=	38.18
Nitrogen	.20364	=	1.921

numbers which very closely correspond with the following formula :

		Theory.	Experiment.
57 Carbon	342 =	36.037	35.8855
38 Hydrogen	38 =	4.004	4.0470
2 Nitrogen	28 =	2.950	2.8510
10 Oxygen	80 =	8.433	8.0625
3 Iodine	381 =	40.147	40.4550
2 Sulphuric acid	80 =	8.429	8.6990
	949	100.000	100.0000

and may thus be provisionally rendered



a formula which closely corresponds with that of the optical salt, but contains 2 atoms less water; it will be shown to bear an equally simple relation to the yellow fibrous silky crystals, from which this greenish black residue was obtained, thus:

The yellow silky fibrous crystals, air-dried, on subsequently heating in Liebig's apparatus during six hours, lost water, and were converted into the olive-coloured residue.

I. 38.55 grs., air-dried, dried at 212° , lost 2.25 grs. HO
= 5.86 grs. per cent.

This experiment was slightly in excess, as the yellow salt was not quite dry.

II. 50.54 grs. more carefully air-dried at 62° , then exposed over SO^3HO in a powdered state, during nine days ceased to lose weight, gave water 2.32 grs., becoming dark olive-coloured, as if it had been heated at 212° .

This residue, after a further exposure during six hours in Liebig's drying apparatus experienced a loss of 0.37 grs.

therefore $2.32 + 0.37 = 2.69 = 5.322$ HO per cent.

which will give the following composition for these crystals:—

Residue previously examined	94.678	= 949	= 1 atom.
Water	.	5.322	53.3 = 6 atoms.

100.000

probably

1 atom residue	949	= 94.616
6 atoms water	54	= 5.384 water

1003 100.000

From the percentages obtained by the analyses of the dry residue, the following proportions will give the subjoined results:—

		In the silky crystals.
Iodine	. . . 100 : 40.455 ::	94.678 : 37.914
Sulphuric acid	100 : 8.699 ::	94.678 : 8.216
Carbon	. . . 100 : 35.856 ::	94.678 : 33.947
Water	. . . 100 : 36.423 ::	94.678 : 34.485 + 5.322
Nitrogen	. . . 100 : 2.851 ::	94.678 : 2.700

We can now compare the results derived from the formula,
+ 6 atoms water.

			Theory.	Experiment.
57 Carbon .	= 342	=	34·097	= 33·947
44 Hydrogen	= 44	=	4·386	= 4·423
2 Nitrogen	= 28	=	2·791	= 2·700
16 Oxygen .	= 128	=	12·764	= 12·800
3 Iodine .	= 381	=	37·986	= 37·914
2 Sulphuric acid	= 80	=	7·976	= 8·216
	<hr/>		<hr/>	<hr/>
	1003		100·000	100·000

giving :

			Experiment.
Carbonic acid . . .		125·022	124·472
Water		39·474	39·807

and, of course, giving the following formula for the yellow silky fibrous crystals,



We are now, therefore, in a position to compare the formulæ for the three varieties of iodo-sulphate of cinchonidine.

a. The optical salt.

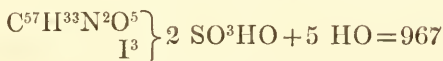
β. The silky yellow fibrous variety.

γ. The dry residue derived from the latter by

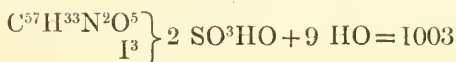
1st. A temperature of 212°.

2nd. By exposure over sulphuric acid.

a. Optical.



β. Silky.



γ. Dry Residue.



consequently, the silky crystals are the optical salt + 4 atoms of water, which, under the influence of excess of sulphuric acid and

prolonged delay at 62°, are assimilated by that salt; this additional water is lost on boiling in spirit, and the optical salt crystallizes on cooling.

If the temperature be not too high *at first*, the silky crystals may be produced without the appearance of the optical salt; and the silky crystals lose 6 atoms of water at 212°, and become the dry residue or tri-hydrate, which, when boiled in spirit '837, also assimilates 2 atoms water, and becomes the optical variety.

Upon reference to the results of the re-examination of the optical salt of quinine, it will be seen that a very striking relationship exists between these salts, thus:—

The formula therein given was—

Quinine Salt.



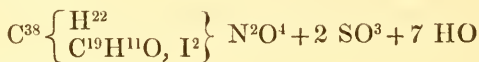
Cinchonidine Salt.



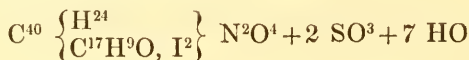
Whence it appears that the only difference between them is the existence of 1 atom of iodine more in the latter salt.

In the case of quinine it has been shown that there was some probability of the introduction of a group $\text{C}^{19}\text{H}^{11}\text{O}$, or $\text{C}^{17}\text{H}^9\text{O}$, into the organic base of the salt to constitute it, thus—

with Laurent,

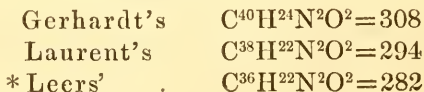


or with Gerhardt,



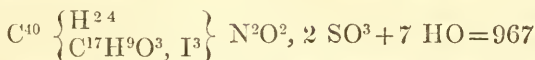
But we have three different formulæ for cinchonidine.

2. Gerhardt's and Laurent's, formed on the assumption that cinchonine and cinchonidine are isomeric, and Leers' from direct analysis of the alkaloid and its salts, thus,

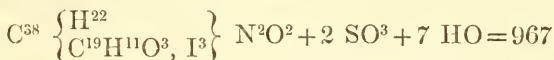


* Ann. Ch. Pharm. lxxxii, 147—a translation of which appears in the Pharmaceutical Journal, December 1852, page 295.

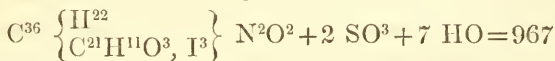
taking Gerhardt's there will be an affixed group of $C^{17}H^9O^3$ to constitute the salt, thus—



according to Laurent, the affix will be $C^{19}H^{11}O^3$, thus—



but, according to Leers, the group will be $C^{21}H^{11}O^3$, thus



It will be seen that under each formula we have O^2 more in the affix than in the corresponding group in the case of quinine; this, of course, is in consequence of the two alkaloids, cinchonidine and quinine, originally differing to that extent in their constitution. It is clear that to obtain these from the splitting of cinchonidine alone would be impossible, as the whole formula contains O^2 only on either supposition; but we have already assumed and proved the assimilation of water; there are, therefore, 2 atoms more water assimilated in this salt, which must be deducted from the true affix derived from the alkaloid itself; they are probably more closely basic than as water of crystallization, whilst the moveable group under either formula differs from that of the quinine salt.

In the present condition of the question, it is impossible to decide upon the true arrangement of the atoms, or even the possible constitution of the salt. One thing is apparent, the striking similarity in the mode of production.

The analysis of the compound with iodide of silver may throw considerable light on this subject.

Process for the preparation of Sulphate of Iodo-Cinchonine.

The alkaloid examined was proved to be free from quinine or quinidine by not showing the slightest green tint with chlorine and ammonia, and to be incapable of producing any golden optical crystals when treated with iodine and sulphuric acid; the difference in its solubility in hot ether distinguished it also from cinchonidine.

Two drachms were dissolved in half an ounce of diluted sulphuric acid, then diluted with 5,000 grs. water, and 10,000 grs. measures spirit '837, it was then raised to 100° Faht., and 81 grs. iodine dissolved in six ounces of spirit.

On repose, black shining prismatic crystals presented themselves, these were allowed some days to fully deposit and gradually

producing the ratio				probably	
Iodine	.	.	·3968	or	3 = 3
Sulphuric acid	.	.	·1308	or	·99 = 1
Carbon	.	.	4·6163	or	34·9 = 35
Hydrogen	.	..	3·487	or	26·36 = 26
Nitrogen	.	.	·236	or	1·79 = 2

				Theory.	Means of Experiments.
35 Carbon	.	.	= 210	= 27·7410	= 27·698
26 Hydrogen	.	.	= 26	= 3·4346	= 3·487
2 Nitrogen	.	.	= 28	= 3·7000	= 3·306
9 Oxygen	.	.	= 81	= 9·5103	= 9·8676
3 Iodine	.	.	= 381	= 50·3301	= 50·4096
1 Sulphuric acid	.	.	= 40	= 5·2840	= 5·232
				757	100·0000



and theoretically requiring

		Expt.	Means.
Carbonic acid	.	101·717	101·552
Water	.	30·9114	31·383

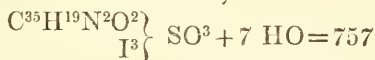
The production of the cinchonine salt appears to depend on the abstraction of carbon and hydrogen from cinchonine, and the introduction of iodine, but in this case 3 atoms of iodine exist for one of sulphuric acid.

Its analogy with the quinidine salt is, therefore, very close indeed, as may be seen by comparing the two proposed formulæ.

The ruby coloured quinidine salt has been shown to consist of



The purple red cinchonine salt is,



and consist individually of the alkaloid as given by Gerhardt, minus C^5H^5 , respectively assimilating in the case of quinidine 2 iodine, in that of cinchonine 3 iodine, and in each instance the salt is a mono-sulphate.

The bases further differ by the existence of 2 atoms of oxygen additional in the quinidine salt, but in this case merely keeping up the difference originally existing between the two isomeric groups.

If, with Laurent, we assume $C^{38}H^{22}N^2O^2$ as the composition of cinchonine, we, of course, only have to account for the loss of C^3H^3 from the organic base in order to constitute the new iodo-base.

We have two cases, therefore, strikingly different from the quinine and cinchonidine salts in their method of constitution.

In conclusion, the author begs publicly to express his thanks to Mr. John Elliott Howard, who most liberally placed at his disposal the necessary quantities of the purified alkaloids, most of which entailed the loss of considerable time and labour in their perfect purification.

XII.—*Some remarks on Poison obtained from Arrows.*

BY HENRY J. B. HANCOCK, Esq.

THE accompanying specimens are of a novel form of what I believe to be the urari, curare, or wourali poison of Guiana, mentioned in the year 1857, by Sir R. H. Schomburgh (Pharm. J. Trans. xvi, 500), and earlier by Mr. Waterton, in his "Wanderings" (3rd edit., p. 84). The idea of extracting it was first suggested to me by my friend, Mr. Pepper, in the summer of the year 1856; and I proceeded to extract it from some poisoned arrows brought from Guiana by Mr. Echlin, who was travelling secretary to Sir R. H. Schomburgh. I deem it curious—

Firstly. On account of the novel form in which it appears.

Secondly. On account of the large quantities in which it was extracted from the arrows.

Thirdly. On account of its preserving to a great extent (as will afterwards appear) its properties, during the many years which elapsed between the arrival of the arrows in England and my experiments.

My method of proceeding was very simple. I steeped the arrows in boiling chloroform, and then scraped them carefully in the same liquid; after evaporating off the chloroform, I obtained the poison mixed with small particles of iron from the scraping; and eventually getting rid of the iron, I obtained a quantity of crystals.

On examination I found that the crystals were nearly insoluble in water, but readily dissolved by chloroform and acetic acid. On testing, I found slight, in fact hardly perceptible traces of the presence of strychnine, but could eliminate nothing further by any test I employed.

I will now proceed to detail its action upon those animals which I have submitted to it.

Some being administered to a frog, no effect was perceptible for the first ten minutes, but after that time the animal became languid, and died in about thirteen minutes from the time of administering the poison, apparently without pain. After death there was none of that rigidity of the limbs which is to be observed after poisoning by strychnine, nor was there anything worthy of remark in the external appearance. And this I take as a proof that the amount of strychnine in the poison is very small, although there may be a slight trace, as pointed out by the tests.

The poison being introduced through an incision in the skin of the back of another frog, the same results followed, but in a shorter time, the frog dying in eight minutes after the operation.

Some of the poison being administered to a cat, the animal walked about as usual for about twenty minutes, and then became languid, repeatedly stretched itself, and at length lying down, died quite quietly, without the least appearance of pain, in about half an hour from the time of administering the poison. After death there was no more rigidity than if the cat had died from natural causes.

XIII.—*On the Composition and Analysis of Black Ash or Ball Soda.*

BY JOSIAH W. KYNASTON,

STUDENT, IN THE LIVERPOOL COLLEGE OF CHEMISTRY.

THE immense importance and extent of the soda manufacture will, it is hoped, be considered a sufficient reason for the publication of the following remarks on the composition of one of the intermediate products. The process of Leblanc, although so extensively and so successfully pursued is, nevertheless, as to several of the products of decomposition, not even now, *after the lapse of nearly sixty years*, thoroughly understood.

Having, at the suggestion of Dr. Muspratt, undertaken an investigation of the whole process, so as if possible to lead to improved modes of manufacture, it appeared of the utmost importance to ascertain with accuracy, the exact composition of black ash or crude carbonate of soda. Several analyses of this highly complex mixture have appeared from time to time, among which may be mentioned those of Richardson, Unger, Brown, Danson, and more recently that of Samuelson, late of this college.

The most striking discrepancy in the several analyses, is in the composition assigned to the *insoluble calcium compound*. The exact constitution of this, has also been a question to which several distinguished chemists have devoted much attention, and on which scarcely two have agreed. Thus, Dumas assumes it to be a combination of two equivalents of sulphide of calcium with one equivalent of lime $2\text{CaS} + \text{CaO}$. Unger, reviewing Dumas' theory of the process of its formation, considers it much more probable that it is a compound of three equivalents of sulphide of calcium, with one equivalent of lime $3\text{CaS} + \text{CaO}$, a formula also assigned to it by Payen, and adopted by the above mentioned analysts; while Rose regarded it as composed of one equivalent of sulphide of calcium, with one of *hydrate* of lime $\text{CaS} + \text{CaO}, \text{HO}$. My analysis appears to me to prove decisively that no such salt as any of the above has any existence in fact; and certainly that the insolubility of the calcareous compound cannot be attributed to its being contained in the ash *in such a state of combination*.

Before stating the reasons for arriving at such a conclusion, opposed as it is to the opinions of such eminent chemists, I will give the method pursued for the determination of the several ingredients, and the calculations founded thereon. The ash examined was kindly supplied to me by Mr. Edmund Knowles Muspratt, and was produced under his superintendence, at the Liverpool Vauxhall Alkali Works. I would here express my acknowledgments to this gentleman for his kindness in explaining to me anything connected with the execution of the process of manufacture. The methods of Brown were adopted in those cases, where they yield accurate results, but in many instances, *they were proved to be quite erroneous*.

To estimate the relative proportions of the soluble and insoluble salts, a portion of the ash was digested for some time in cold water, afterwards thrown on a weighed filter, and washed. The results can only be considered as approximate, as by continued affusion,

after the extraction of the salts of soda, the filtrate still continues alkaline. This alkalinity is owing to the presence of caustic lime, produced by the decomposition of the sulphide of calcium, which, by exposure to the air, is gradually decomposed into sulphide and bisulphide of calcium, and caustic lime $3 \text{CaS} + \text{O} = \text{CaS} + \text{CaS}_2 + \text{CaO}$. If the washing with exposure be still further continued, the sulphur becomes oxidised, giving rise to sulphite and hyposulphite of lime, and lastly to sulphate of lime, all of which pass through the filter. In the estimation, the washing was discontinued on the first appearance of lime in the filtrate. The residue dried at 212° gave 59 per cent. as the amount of insoluble matter, and consequently 41 per cent. of soluble salts.

To determine the respective quantities of lime and soda, 1.954 grammes were taken, and treated with hydrochloric acid. The filtrate was neutralized with ammonia and again filtered. From this solution, the lime was thrown down by oxalate of ammonia, and the oxalate of lime collected, washed, dried and ignited, yielded 1.225CaO , $\text{CO}_2 = 35.109$ per cent. CaO . This lime as subsequently calculated, exists in the ash as follows:—

$$\begin{array}{rcl}
 22.307 & = & 15.934 \text{ Ca as CaS} \\
 & & 1.8564 \text{ as CaO, CO}_2 \\
 0.2344 & = & 0.1674 \text{ Ca as CaS}_2 \\
 0.4245 & \text{ as } & \text{CaO, S}_2\text{O}_2 \\
 1.0164 & \text{ ,, } & \text{CaO, SO}_2 \\
 9.2703 & \text{ ,, } & \text{CaO} \\
 \hline
 35.1090 & &
 \end{array}$$

The filtrate from the oxalate of lime was acidulated with hydrochloric acid, and evaporated to dryness, to remove silica. The chloride of sodium was converted into sulphate, and the weight of the latter was $1.075 = 24.024$ per cent. NaO contained in the ash as follows:—

$$\begin{array}{rcl}
 21.5705 & \text{ as } & \text{NaO, CO}_2 \\
 1.348 & = & .0994 \text{ Na as NaCl} \\
 0.1726 & \text{ as } & \text{NaO, SO}_3 \\
 0.6734 & \text{ ,, } & \text{NaO, SiO}_2 \\
 0.2595 & \text{ ,, } & \text{NaO, Al}_2\text{O}_3 \\
 \hline
 24.0240 & &
 \end{array}$$

The centesimal amount of soda, as carbonate, silicate, and aluminate was also estimated volumetrically by means of a test acid. It yielded 22·5 per cent.

Another larger portion of the ash, 6·562 grammes, was taken, and in this quantity were determined the ultramarine, silica, charcoal, protoxide of iron (as FeS), alumina (as NaO , Al_2O_3), and magnesia. This was digested with successive portions of *warm* water, until the soluble portion was completely extracted. The dark green aqueous solution was boiled until the ultramarine had deposited. This was filtered off, washed, dried, and ignited, and gave 0·9589 per cent.

The filtrate from the ultramarine was acidulated with hydrochloric acid, and boiled, then neutralized with ammonia. The precipitate of alumina thus obtained gave 0·4291 per cent. The filtrate from the last precipitate was again acidulated with hydrochloric acid, and evaporated to dryness, and the residue treated with water, left silica amounting to 0·5086 per cent.

The portion of ash insoluble in water was then treated with very dilute hydrochloric acid, and after expulsion of sulphide of hydrogen, thrown on a weighed filter. From the filtrate, oxide of iron, alumina, and phosphate of lime were thrown down by ammonia. In this precipitate, the iron was estimated by means of permanganate of potassa, and yielded 0·3372 per cent. of Fe_2O_3 .

After having removed lime from the filtrate, by means of oxalate of ammonia, the magnesia was precipitated by phosphate of soda, and afforded 0·2537 per cent. of MgO .

The residue, undissolved by hydrochloric acid, was dried at 212° and the weight noted. From this, the charcoal was removed by long continued ignition, and calculated from the loss of weight sustained. It gave 7·007 per cent.

In another portion of ash, 5·543 grammes, the sand, and total amount of sesquioxide of iron, alumina, and phosphate of lime were determined. In this case, the ash was treated with dilute hydrochloric acid, and after expelling sulphide of hydrogen, the liquid was decanted. The residue was then boiled with aqua regia until only the sand remained. The latter dried, ignited, and weighed, gave 0·901 per cent. The two acid solutions were then mixed, and precipitated by ammonia. From the precipitate redissolved in hydrochloric acid, the alumina was removed by excess of potassa. The precipitate of sesquioxide of iron and phosphate of lime thus obtained, gave 2·9952 per cent. From this is subtracted the sesquioxide of

iron, obtained by solution of the ash in dilute acid, and which is assumed to exist as FeS ; the residue 2.658 expresses the quantity of anhydrous sesquioxide of iron and phosphate of lime.

The alumina was thrown down from the potassa solution by ammonia, after treating with hydrochloric acid and chlorate of potassa. The percentage was 1.5609. Subtracting from this, the alumina existing as NaO , Al_2O_3 which is soluble in water, the residue gives 1.1318 as the proportion of anhydrous alumina.

In another portion of ash, 21.4 grammes, sulphuric acid was estimated after treating with hydrochloric acid, by precipitation as sulphate of baryta, and gave 0.2228 per cent. SO_3 .

The total amount of sulphur was determined by fusing 2.131 grammes of ash with three or four times its weight of nitrate of potassa, treating the fused mass with dilute acid and water, and precipitating sulphuric acid from the filtrate by chloride of barium. The total percentage of sulphur was 14.565.

The amount of sulphur existing in the insoluble state was also determined in the same manner as the preceding, the soluble portion having been previously extracted by repeated washing. 1.546 grammes were taken, and yielded 12.882 per cent.

The process adopted for the estimation of sulphur as soluble bisulphide, hyposulphite, and sulphite was founded upon the following reactions. Carbonate of cadmium is decomposed by a solution of alkaline sulphide, yielding sulphide of cadmium and carbonate of the alkali. Nitrate of silver, mixed with solution of hyposulphite of soda, affords hyposulphite of silver. When heated in water, the latter is decomposed into sulphide of silver and sulphuric acid, AgO , $\text{S}_2\text{O}_2 = \text{AgS} + \text{SO}_3$.

The same salt added to a soluble sulphite gives sulphite of silver; and this also on heating with water is decomposed, yielding sulphuric acid and metallic silver AgO , $\text{SO}_2 = \text{SO}_3 + \text{Ag}$.

In the two latter decompositions, it will be observed that a quantity of sulphuric acid is produced, one equivalent of which is equal to one either of sulphite or hyposulphite.

The analysis was conducted as follows:—3.463 grammes of ash were exhausted with cold water. To the filtrate, a quantity of freshly prepared and still moist carbonate of cadmium was added, and the mixture was digested, with frequent agitation, till the alkaline sulphide was decomposed. The precipitate of sulphide and carbonate of cadmium was then filtered off, and treated with dilute acetic acid to remove undecomposed carbonate; the residual

sulphide was oxidized by fuming nitric acid, water added, and the sulphuric acid produced was then estimated as sulphate of baryta; calculated as sulphur, it gave 0.2679 per cent.

To the filtrate from the cadmium salts, nitrate of silver was added, and the mixture maintained at a temperature approaching ebullition, until the sulphite and hyposulphite were decomposed, indicated by the successive changes in the colour of the mixture. The precipitate of carbonate, sulphide, and metallic silver was then filtered off, and treated with ammonia to remove the carbonate. The sulphide was then oxidized by fuming nitric acid, and the sulphuric acid precipitated as sulphate of baryta; from the weight of the latter the quantity of hyposulphite was calculated; it gave 0.4852 per cent. of sulphur, existing in this condition.

In the filtrate from the silver precipitate the sulphuric acid was estimated as BaO , SO_3 ; and deducting that originally existing in the solution, and that formed from the decomposition of hyposulphite, the residue was calculated as sulphurous acid, giving 0.5808 per cent. of sulphur existing in this state.

The several determinations of sulphur, therefore, give the following results:—

Total percentage of sulphur 14.565.

Sulphur insoluble . . .	12.882	{ including 0.135 as FeS
„ as soluble bisulphide .	0.2679	
„ „ hyposulphite	0.4852	
„ „ sulphite .	0.5808	
„ „ sulphate .	0.0891	
	<hr/> 14.3050	

The amount of carbonic acid was arrived at by two distinct operations. 3.531 grammes of ash were digested with successive portions of water, to remove the soluble salts. In this solution, the carbonic acid was estimated by a Fresenius' and Wills' apparatus, with addition of a quantity of neutral chromate of potassa to oxidize the sulphur compounds. It yielded 9.6832 per cent. The residue insoluble in water was transferred to a retort, and treated with hydrochloric acid. The gas evolved was passed into a mixture of chloride of calcium and ammonia. The precipitate

of carbonate of lime thus obtained, was collected, washed, and introduced also into a Fresenius' and Wills' apparatus, and the carbonic acid liberated by nitric acid. It gave 8·6698 per cent.

The above was found to be the only practicable method for effecting this determination. An attempt was made to estimate this acid at once, in a Fresenius' and Wills' apparatus; but the addition of a large excess of chromate of potassa, and even of permanganate, failed to oxidize the sulphur compounds. Nor could the operation be effected by treating the ash at once with acid, and conducting the evolved gases into a solution of chloride of calcium and ammonia, as the sulphite of lime formed would introduce another error. The sulphur salts existing in the aqueous solution, were readily and completely decomposed by chromate of potassa.

Another process suggested, was to oxidize the sulphite of lime, formed when the evolved mixture of gases was conducted into the chloride of calcium solution, and to deduct the sulphite found from the original weight of the precipitate; but as it was necessary to ascertain exactly the proportion of carbonic acid in the state of carbonate of lime, the process already given was adopted.

Chlorine was estimated by treating 2·841 grammes of ash with nitric acid, expelling sulphide of hydrogen, &c., and precipitating the filtrate by nitrate silver. It gave 1·533 per cent.

Lastly, the hygroscopic moisture was determined by heating a portion of ash to about 300°. It indicated 0·2158 per cent.

From the above analysis, now given in a tabular form, the percentage composition was calculated.

Soluble salts	41
Insoluble matter and salts	59
					<hr/>
					100
Lime	35·109		
Soda	24·024		
Ultramarine	0·9589		
Silica	0·5086		
Magnesia	0·2537		
Charcoal	7·007		
Sand	0·901		
Sesquioxide of iron and phosphate of lime	}		..	2·9952	{ including 0·3372 Fe ₂ O ₃ existing as FeS

Alumina	1.5609	{ including 0.4291 as NaO, Al ₂ O ₃
Sulphuric acid ..	0.2228	
Total amount of sulphur ..	14.565	
Carbonic acid ..	18.353	{ soluble 9.6832 insoluble 8.6698
Chlorine	1.533	
Water	0.2158	

Percentage Composition.

Carbonate of soda	36.8786
Chloride of sodium	2.528
Sulphate of soda	0.3954
Silicate of soda	1.182
Aluminate of soda	0.6886
Sulphide of calcium	28.681
Carbonate of lime	3.3151
Bisulphide of calcium	0.4353
Hyposulphite of lime	1.1523
Sulphite of lime	2.178
Caustic lime	9.2703
Magnesia	0.2537
Sulphide of iron	0.3710
Sesquioxide of iron and phosphate of lime	2.658
Alumina	1.1318
Charcoal	7.007
Sand	0.901
Ultramarine	0.9589
Water (hygroscopic).. ..	0.2158

100.2018

It will be seen in the preceding analysis, that the lime is calculated as existing in several combinations of sulphur, and as carbonate and caustic lime. The reasons for this will be apparent from a study of the analysis. Thus, it will be observed, that in the determination of the carbonic acid, 8.66 per cent. was found to exist in the compound *after treatment with water*, as carbonate of lime, while 22.307 per cent. = 15.934 of calcium, is shown to

exist as sulphide of calcium, CaS , the proportion of sulphur remaining insoluble after deducting that combined with iron, as FeS , being the quantity required to produce CaS . Therefore, it is evident, that in the portion of the ash insoluble in water—that is to say, in soda waste, no lime exists, either combined with CaS , or in the free state.

It must, however, be acknowledged, that this analysis does not disprove the presence of some such compound in the ash, as removed from the furnace, and *before treatment with water*. But, why assume the existence of such a compound, and what end is to be served? Dumas, when showing the necessity of adding a quantity of lime above that required to produce CaS , says:—“But it must yet be observed, that if only two atoms of chalk be used, on dissolving in water, the sulphate of lime converted into sulphide of calcium by the charcoal, will be decomposed by the carbonate of soda, and the result will be the reproduction of the the chalk, together with sulphide of sodium. On this account, three atoms of chalk are used, because, then one atom of lime remains free, and uniting with the two atoms of sulphide of calcium, produces a compound insoluble in cold water. Thus, only the carbonate of soda dissolves, and entirely escapes decomposition by the sulphide produced.”

From the above extract, it is evident, that Dumas assumes the existence of his $2\text{CaS} + \text{CaO}$, because the additional atom of lime has the effect of rendering the CaS insoluble; and this fact is generally adopted by others, as a proof of the existence of this or a similar compound, and certainly the conclusion seems a very plausible one. But if, by treatment with water in contact with the alkaline carbonate, it is found that the lime supposed to be combined with sulphide of calcium is removed from it and converted into carbonate, with simultaneous production of the objectionable compound, then what becomes of the theory, when the very fact that led to its adoption is shown to be erroneous?

Unger, besides the above, reasons from analogy, and considers that because Rose, on leaving a baryta solution *for some years* in a bottle, obtained a compound, having the formula $3\text{BaS} + \text{BaO} + 28\text{HO}$, that, therefore, the compound $3\text{CaS} + \text{CaO}$ might reasonably be supposed to exist. But, what analogy is there between the two compounds? Were the above baryta compound known in the anhydrous condition, $3\text{BaS} + \text{BaO}$, then we might reasonably assume the existence of the corresponding salt,

$3 \text{CaS} + \text{CaO}$. But this is unknown, and therefore, the analogy falls to the ground.

But, it will be asked, how then does the additional atom of lime render the CaS so insoluble? I must confess, I am not quite prepared with an answer to this question; but would say in reply, is it not as rational to suppose that an atom of carbonate of lime may unite with the CaS , to produce a difficultly soluble compound $2 \text{CaS} + \text{CaO}, \text{CO}_2$? If we adopt this opinion, and suppose that combination immediately ensues on treating the ash with water, all difficulty is at once removed.

In the examination of another sample of ash, the annexed results were obtained:—

Carbonic acid as carbonate of lime	8.993	per cent.
Total quantity of lime	35.348	„
Sulphur in the insoluble state ..	12.768	„

These determinations give the following results:—

Lime = 15.96 calcium as sulphide	22.344 = 28.728	CaS
„ as carbonate of lime. . . .	11.445 = 20.438	CaO CO_2
„ „ caustic	1.659	

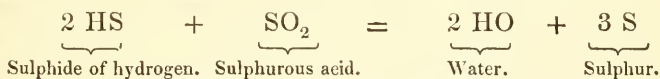
The above, although a small quantity of lime remains free, is *another proof of the non-existence of any of the hitherto assumed compounds*, but is not inconsistent with the theory broached above, the quantity of CaS there given, requiring 19.95 CaO, CO_2 to form $2 \text{CaS} + \text{CaO}, \text{CO}_2$.

Another explanation of the fact, why the additional quantity of lime should prevent the solution of the sulphide, is by supposing that the excess of lime prevents the formation of bisulphide, as, in my opinion, only the bisulphide, and not protosulphide of calcium, is decomposed by the solution of alkaline carbonate. If the supposed compounds of Dumas and Unger are more stable than sulphide of calcium, why are they so readily decomposed by exposure to the air, as is shown in the decomposition proved to take place in the extraction of the soluble salts, and how is it that the products of this metamorphosis are precisely those which occur in CaS under similar circumstances?

By Unger and others, a large quantity of hydrate of soda has been found; I believe *no caustic soda can possibly be produced*, and certainly from Unger's own results, none is proved to exist, although he has calculated it in this condition. It has been

suggested that NaO may be produced by the expulsion of carbonic acid from the carbonate of lime, and a subsequent decomposition of the CaO, and sulphide of sodium; $\text{CaO} + \text{NaS} = \text{CaS} + \text{NaO}$. But, according to the theory of Dumas, the sulphate of soda first decomposes with carbonate of lime, forming carbonate of the alkali, and sulphate of lime, and this salt is afterwards reduced to sulphide of calcium by the charcoal. In this case, no sulphide of sodium can have been formed, and as carbonic acid once combined with soda cannot be again removed by simple heating, of course *no caustic soda can be produced*.

Whether a sulphite and hyposulphite actually exist is a question that hardly admits of proof, though my researches would certainly lead to the conclusion that they do; for, on treating with cold water, the first washings were found to contain sulphide, sulphite, and hyposulphite, though I allow the possibility and even probability of the formation of these, subsequent to the removal of the black ash from the furnace. In the experiment last given, another curious fact was observed, viz. the existence, simultaneously, of sulphurous acid, and sulphide of hydrogen. Sulphurous acid was distinctly perceptible by its pungent and peculiar odour, on adding hydrochloric acid, while lead-paper was blackened by the gas eliminated. Of course the two gases collected would mutually decompose in the subjoined manner:—



Many eminent chemists have asserted, that the two gases could not be collaterally evolved; but this, as Dr. Muspratt affirms, is placed beyond a doubt by his own experiments and by mine.

NOTE.—The sample of ball-soda operated upon by the author had probably been exposed for a considerable time to the air; since it is well known that the lixivium obtained in the ordinary mode of treating ball-soda, always contains a considerable proportion of caustic alkali, the presence of which would probably interfere with the application of the author's new methods of analysis to the determination of the sulphides, hyposulphites, &c., in such lixivium.—[ED.]

XIV.—*Process for the quantitative estimation of Sulphides, Sulphites, Hyposulphites, and Sulphates, in presence of each other, as adopted in the determination of these salts in "Soda Waste," as obtained from "Black Ash."*

BY J. W. KYNASTON,

STUDENT IN THE LIVERPOOL COLLEGE OF CHEMISTRY.

THIS method is founded upon the decomposition of an alkaline sulphide by carbonate of cadmium; $\text{CdO}, \text{CO}_2 + \text{NaS} = \text{CdS} + \text{NaO}, \text{CO}_2$, and on the changes produced in hyposulphite of silver, and sulphite of silver when heated in water nearly to boiling, which may be expressed thus:— $\text{AgO}, \text{S}_2\text{O}_2 = \text{AgS} + \text{SO}_3$, and $\text{AgO}, \text{SO}_2 = \text{Ag} + \text{SO}_3$. By means of the above reactions, these sulphur salts may be estimated without difficulty, and with positive certainty, as is proved by the subjoined experiments.

To overcome the difficulty of obtaining a sulphide containing a definite proportion of sulphur, 100 measures of a very dilute solution of sulphide of ammonium were taken. In 50 measures, the proportion of sulphur was estimated by precipitating as sulphide of copper. The sulphide was oxidized by nitric acid, and the sulphuric acid precipitated as sulphate of baryta, and yielded 3·7364 grammes $\text{BaO}, \text{SO}_3 = 1\cdot0904$ of protosulphide of ammonium NH_4S . The other half of the solution, of course containing the same amount of sulphide, was reserved for estimation in admixture with the other salts. A similar difficulty arises in obtaining a sulphite of definite composition, and this was overcome in a similar manner. A neutral solution of sulphite of soda was prepared, and 100 measures taken, in half of which the sulphite was estimated—after oxidizing by means of chromate of potassa, and acidifying—by precipitating sulphuric acid with chloride of barium. The weight of BaO, SO_3 obtained was 0·6502 grammes = 0·3516 of sulphite of soda NaO, SO_2 . The other 50 measures, representing the same weight of sulphite, were added to the solution of sulphide of ammonium. Afterwards, 1·146 grammes of crystallized hyposulphite of soda, pulverized, and pressed in bibulous paper, were dissolved and added to the mixture, and lastly 1·213 grammes of anhydrous sulphate of soda. Thus was produced a solution containing 1·0904

grammes NH_4S ; 0·3516 of NaO , SO_2 : 1·146 of NaO , S_2O_2 ; and 1·213 grammes of NaO , SO_3 ; which would afford a mixture, having the following percentage composition:—

Sulphide of ammonium	.	.	28·687
Sulphite of soda	.	.	9·250
Hyposulphite of soda	.	.	30·150
Sulphate of soda	.	.	31·913
			<hr/>
			100·000

To this mixed solution, a quantity of carbonate of cadmium was added, and the whole was digested for some time, with frequent agitation. The mixture of sulphide, and undecomposed carbonate of cadmium was then filtered off, and treated with acetic acid to remove the latter salt. The residue of CdS was then treated with nitric acid. Only a portion of the sulphur was oxidized: the residue was collected by filtration, dried and weighed, giving 0·3205 grm. of sulphur. From the nitric acid solution, the sulphuric acid was thrown down as sulphate of baryta, and the weight of the latter was 1·3782 grammes. This and the separated sulphur represent 1·0833 of NH_4S = 28·5004 per cent.

To the filtrate from the cadmium salts, nitrate of silver was added as long as a precipitate was produced. The mixture was heated nearly to ebullition, and kept for some time at that temperature. The silver precipitate was then collected, washed, and partially dried, then treated with concentrated nitric acid. The whole of the sulphide was oxidized, and the sulphuric acid formed, was precipitated as sulphate of baryta, giving 1·0732 grammes = 1·1423 NaO , S_2O_2 + 5 HO = 30·0526 per cent.

The sulphuric acid in the filtrate from the silver precipitate, was thrown down as sulphate of baryta, and yielded 3·7276 grammes. Subtracting from this 1·9889 = the quantity of NaO , SO_3 present, and 1·0732 = the NaO , S_2O_2 , 5 HO , found above, the residue represents the quantity of NaO , SO_2 .

Total weight of BaO , SO_3	.	.	3·7276
BaO , SO_3 = 1·213 NaO , SO_3	.	.	1·9889
			<hr/>
			1·7387
,, = 1·1423 NaO , S_2O_2 + 5 HO	.	.	1·0732
			<hr/>
= BaO , SO_3 NaO , SO_2 remaining	.	.	0·6655

This residue, 0·6655 BaO, SO₃ represents 0·3598 of NaO, SO₂ = 9·4659 per cent.

There are found therefore :—

Sulphide of ammonium . . .	28·5004
Sulphite of soda . . .	9·4659
Hyposulphite of soda . . .	30·0526
Sulphate of soda . . .	31·9130
	<hr/>
	99·9319

I now append the numbers collaterally, to prove at a glance the accuracy of the methods employed :—

	Theory.	Analysis.
Sulphide of ammonium . . .	28·687	28·5004
Sulphite of soda . . .	9·250	9·4659
Hyposulphite of soda . . .	30·150	30·0526
Sulphate of soda . . .	31·913	31·9130
	<hr/>	<hr/>
	100·000	99·9319

This process answers equally well in presence of a large proportion of alkaline carbonate; but in this case, it is necessary to treat the silver precipitate with liquid ammonia to remove carbonate of silver, previous to the oxidation of the sulphide.

XV.—Remarks on Metallic Deposits found in two Chimneys attached to Reverberatory Furnaces, one being used for Melting an Alloy of Silver and Copper, and the other an Alloy of Silver and Gold.

BY JAMES NAPIER, ESQ, JUN.,

CHEMIST AND ASSAYER TO THE GUANÀXUATO MINT, MEXICO, AND LATE IN THE LABORATORY OF ST. THOMAS'S HOSPITAL, LONDON.*

IN a paper which Dr. Thomson was kind enough to communicate for me to the society in June of last year,† I endeavoured to point out from our every day experience, and from experiments, that gold (even in its pure state) when fused and exposed, in that condition, to the ordinary temperature of our melting furnaces is like most other metals volatile; but Mr. C. J. Devey, of Birmingham, in the Mining Journal of the 31st March, 1855, goes as far as to

* Communicated by Robert Dundas Thomson, M.D., F.R.S.

† Chem. Soc. Journ. x. 229.

state that gold does not require even to be melted to volatilize, but to be heated only to a good red heat. This experiment I have tried repeatedly, keeping thin slips of pure gold (about 2 inches in length and $\frac{1}{2}$ an inch in breadth) at a good red heat for 10 hours at a time, but never found the slightest diminution of weight, although the gold operated upon became very soft, and as ductile as a piece of lead, and the surface was covered with small *blisters* (if we may use the term). It is probable that the gold used by Mr. Devey, for his experiments, was contaminated with some other metal, which carried off the gold.

I hope by the following facts to be able to point out clearly the great danger of melting the precious metals in open furnaces, without some contrivance for the condensation of the whole of the soot, &c. which passes up the chimney, and also to show that volatilization is one of the *great* causes of loss in melting these metals on the large scale.

The following table shows the analyses of deposits taken from the *top*, *middle*, and *bottom* of a chimney, about 35 feet high, attached to a small reverberatory furnace, in which is melted almost daily, for months together, an alloy of silver and copper (silver coin) with a small portion of gold, so small as not to pay for its extraction in this country (Mexico); the average proportion of this metal will not exceed 3 grains per mark (8 ounces) of alloy, and in no instance does the alloy contain as much as 8 grains of gold per mark. During the whole of the time, from 2 to 3 hours, the alloy is in the melted state its surface is thickly covered with charcoal.

Substances found.	Bottom.	Middle.	Top.	Mean.
Metallic silver	29·950	9·190	3·300	14·170
Oxide of silver	·170	5·210	7·180	3·186
Metallic copper	2·800	·250	·120	1·066
Oxide of copper	1·930	·740	·150	·940
Oxide of iron and alumina	7·300	11·430	10·390	9·706
Cub. lime and magnesia	43·850	48·720	52·690	48·420
Silica	14·000	23·510	24·220	20·576
Carbonaceous matter	·960	1·260	·740
	100·000	100·010	99·310	98·804
Total metallic silver	30·056	12·461	7·808	16·775
Total metallic copper	4·344	·842	·240	1·808
Grs. of Gold per mark of silver	8·	7·3	6·	7·1

A quantity of soot was also collected, as it escaped, about 4 feet

from the top of the chimney, and on examination it was found to contain 3 per cent. of silver, with also a small portion of gold. Soot deposited on a wall against which the chimney stands was found to contain 4·2 per cent. of silver, which silver contained also gold.

Such results require no comment to show the large loss of silver sustained in melting this metal in open reverberatory furnaces.

On referring to the above table of analyses, it will be seen that as we ascend the chimney, the oxide of silver increases in amount, and this from the character of the metal, and taking all circumstances to which it is exposed into consideration, is what we might expect. I think there is little doubt that the silver is volatilized in the metallic state, for the deposit from the three parts of the chimney, when examined through a lense, is found to be perfectly full of very small particles of silver—almost an impalpable powder; but when this deposit remains for a time in contact with the air, and is exposed only (while the furnace is working) to a gentle heat, the silver is partly converted into oxide; the top of the chimney being most exposed to the action of the atmosphere and a gentler heat, it is there we might expect, and do find, the most oxide of silver. At the bottom, on the contrary, we find only a small portion of oxide, and this I conceive is, because this part of the chimney is, when the furnace is working, always at a *strong* red heat, and oxide of silver, I think, will neither form nor exist under the influence of a strong red heat; the small portion of oxide of silver found at the bottom, is probably formed after the fire is extinguished, and the deposit cooled in a current of hot air.

From the above analyses, and from observation, I am led to suppose that most of the copper also passes off in the metallic state *combined with the silver as alloy*—that is to say, although copper of itself is not volatile in the metallic state, it can, when combined with another metal, which is so, such as silver, be carried off in that form, and like silver is partially converted into oxide after deposition; in fact there is no other way by which I can account for the presence of metallic copper, as there is no circumstance under which the deposit is placed in the chimney, by which *oxide* of copper (had it passed off in that form) could have been converted into the metallic state, the circumstances tending to the opposite result.

The presence of the metallic copper is also a stronger proof of

the silver having been carried away as metal, and not, as a celebrated chemist has lately supposed, in the form of an oxide, which according to his theory, would be reduced after deposition. If we suppose that the silver actually volatilized as oxide, and afterwards became reduced in the chimney, it would be impossible that such silver could contain copper in the metallic form, for it is well known that this latter metal, when alone, in fusion will pass off in no other state than that of an oxide. Moreover the two metals would not be found as an alloy, as they are, but separate; from these facts I think it natural to suppose that both metals have been carried away, in the metallic form, but I have no doubt that a small portion of the *copper* does pass off as oxide.

At the bottom of the chimney, the deposit naturally contains the largest percentage of oxide of copper, for the greater the heat to which this metal is exposed, the greater tendency has it to oxidize.

The next, and perhaps the most extraordinary feature in these analyses, is the presence of gold in such large quantities, the amount being at least double that which originally existed in the alloy. The presence of gold in this deposit was not so much calculated to excite surprise, after having proved that this metal when pure was to a certain extent volatile, when kept in fusion; but I was much puzzled, and at a loss to account for the presence of a larger quantity than originally existed in the melted alloy. It occurred to me, from results stated in my paper of last year,* that the copper was the agent which carried the gold away in such undue proportions, as the affinity of these two metals for each other is very great.

To endeavour to explain this however, I made the following experiments. In the first place, I obtained a piece of silver containing by assay, 1116 grains of gold per mark—no other metal—and kept it in a fused state for five hours, its surface being covered with charcoal; at the end of this time it was removed from the fire, and again assayed for gold, when it was found to have increased to 1141 grains per mark, showing that the volatilized portion (for it lost in weight) did not contain so much gold as the original alloy.

Secondly. I prepared a piece of alloy having—

1000 grains of gold per mark of alloy, 11 per cent. of copper, and the remainder silver.

* Chemic. Soc. Journ. x, 231.

This was fused, and kept so, with its surface covered with charcoal, for $3\frac{1}{2}$ hours, after which, it gave of gold only a trifle under 1000 grains per mark. These experiments were repeated various times, with alloys containing from 4 grains to 1000 grains of gold per mark, and the same result was always obtained.

Although these experiments do not clearly prove why the silver in the refuse should have more gold than the alloy melted in the furnace, I am still of opinion that the copper is the cause, and there may be circumstances unknown to us to which the alloy is exposed in the furnace, which do not operate on the small scale. However, in all cases where copper was present in the above experiments, the alloy after fusion *always* contained a little less gold than before fusion.

I may here refer to a few facts observed in conducting these experiments, which may not be void of interest. The above alloys when in fusion, were always, as stated, kept covered with charcoal; if this be avoided, and the same operation gone through, the result obtained is very different.

For example, an alloy containing—

842 grains of gold to the mark of alloy,

20 per cent. of copper,

and the remainder silver, was kept in fusion for an hour and a half without charcoal or other carbonaceous matter, when it was again assayed, and gave 855 grains of gold per mark, showing an augmentation in gold, to the extent of 13 grains per mark. There was formed on the surface of the alloy during fusion, a crust of oxide of copper, which when examined, contained a third of its weight of *metallic* silver—not a trace of oxide—and what is most singular, only the smallest trace of gold; and the silver under the crust of oxide, contained only a trace of copper. Here we have a proof of the little tendency which gold has to combine with oxide of copper, although it is most difficult to free gold from metallic copper by fire. A short time since, an extraordinary instance of the affinity of gold for copper, occurred in a metallurgical work in this country. An ore containing sulphide of silver and copper, with also gold, was treated by the barrel process of amalgamation, to obtain the gold and silver. In the calcination of the ore with common salt, some of the copper was converted into sulphate, which, when introduced into the barrels with iron, was reduced to the metallic state, and combined with the mercury, and there was formed an amalgam of copper and silver. This amalgam was freed

from mercury in the usual way, by burning under a copper bell,—but mark the result; when the burning was concluded, the bell removed, and the mass examined, it was observed that it had separated into two parts in burning. The outer surface or crust, was white, and had the form of a cauliflower, and contained—

Silver	74·15
Copper	25·52
Gold	·33
			<hr/>
			100·00

whilst the interior part was brown, and gave by analysis—

Silver	4·00
Copper	61·97
Gold	.	..	34·03
			<hr/>
			100·00

The next table shows the analyses of deposits taken from a chimney, about 35 feet high, attached to a small reverberatory furnace, used for melting an alloy of silver and gold for granulation, previous to its being dissolved in sulphuric acid to obtain the gold. The melted metal is not as in the previous case covered with charcoal, but there is kept floating about on its surface a number of bone-ash cupels, for the purpose of absorbing small quantities of lead, which at times exist in some of the silver operated upon.

The deposits taken from the bottom, middle, and top of the chimney, gave by analysis the following results:—

Substances found.					Bottom.	Middle.	Top.	Mean.
Metallic silver	48·750	39·160	29·380	39·096
Oxide of silver	·032	3·140	1·982	1·718
Metallic copper	·250	·250	·166
Oxide of copper	·750	·125	·125	·333
Gold	4·250	2·640	2·120	3·003
Oxide of lead	slight trace	2·200	2·800	1·666
Oxide of antimony	·091	·111	·067
Carbonaceous matter	trace	3·390	4·200	2·530
Insoluble in acid	25·300	26·500	33·900	28·566
Lime, magnesia, iron, and aluminum	19·918	22·304	24·332	22·188
					<hr/>	<hr/>	<hr/>	<hr/>
					99·000	99·800	99·200	99·333
					<hr/>	<hr/>	<hr/>	<hr/>
Total metallic silver	48·779	42·083	31·225	40·695

Here again, we have an undeniable proof of the great loss sustained by the volatilization of the precious metals; and when we remember that it is only that portion of the metallic substance which touches the sides of the chimney, that has any chance of being recovered by deposition, we can at once see the great necessity there is, on the part of those engaged in the reduction or melting of the precious metals on the large scale, either to employ some means for the prevention of such loss, or to devise some kind of condensing chambers to retain the volatilized metal.

Guanàxuato Mint (Mexico),

March 26th, 1858.

XVI.—*Notes on the Action of Oxidising Agents on Sulphocyanides.*

By E. A. HADOW, Esq.

DEMONSTRATOR OF CHEMISTRY IN KING'S COLLEGE.

HAVING had occasion to estimate approximately the amount of sulphocyanide contained in a certain solution, the plan adopted as being most speedy was that of estimating it by its power of decolorising, when acidulated, a solution of permanganate of potash, previously graduated by pure sulphocyanide of potassium. In doing so, I was struck with the large amount of permanganate, decolorised by a given weight of sulphocyanide, compared with that required by a similar weight of metallic iron, for the graduation of the ores of which, the solution had originally been prepared; and I was inclined to imagine at first that an entire oxidation of all the elements must have been brought about; but on actually estimating the amount of oxygen imparted by the permanganate, it was found to be only between 5 and 6 atoms of oxygen for every atom of sulphocyanogen, a quantity sufficient for the oxidation of the sulphur alone, without any surplus for attacking the hydrocyanic acid, with which it was then not difficult to perceive that the solution abounded. It appears surprising that a body like hydrocyanic acid, related as it is to formic acid, should resist a powerful oxidizing agent, like permanganate of potash, better than the sulphur with which it was in combination; but such is the case; and not only so, even a strong solution of permanganate has no apparent action on hydrocyanic acid of Scheele's strength, *pro-*

vided the mixture is acidulated by some stronger acid; if, on the other hand, the mixture is neutral or alkaline, instant decomposition and decoloration ensues. The ease also with which the sulphur of sulphocyanides is oxidised is not less remarkable, it being by no means necessary to use such a powerful agent as permanganate of potash. Black oxide of manganese rapidly attacks the sulphur of even a very dilute solution of a sulphocyanide, when acidulated, and so it might be concluded would bichromate of potash, a fact which I had incidentally observed on a former occasion, while estimating the carbonic acid in a sample of gas lime, when, in order to prevent the escape of sulphurous acid, (from the hyposulphites which were present,) together with the carbonic acid, some bichromate of potash was added to the mixture; it was then noticed, while sucking out the carbonic acid after the operation was over, that there was a strong flavour of hydrocyanic acid in the gas drawn out. Peroxide of lead, like the other reagents, has no effect on neutral sulphocyanides; any acid, however, even acetic, instantly renders it active, and it immediately turns white from formation of sulphate of lead. It is necessary, at the same time, to remark, that simple as the ultimate action of oxidising agents appears to be, it evidently passes through various complex stages, which are perceptible enough when permanganate of potash is used, the first portion is rapidly and perfectly decolorised, but, after a certain point, the red of the permanganate instead of instantly disappearing, passes through shades of yellow and brown before finally becoming colourless, and, lastly, peroxide of manganese is precipitated. This is not due to gradual diminution of sulphocyanide, for then dilution ought to produce the same result, which it does not, but to the successive oxidation of distinct products, and if the solutions be used concentrated, a yellow body, (probably pseudosulphocyanogen) is precipitated. This does not however explain the decomposition; for, as sulphuric acid makes its appearance from the very first, while there is but little hydrocyanic liberated until quite towards the last—there must be some cyanogen compound formed, containing less sulphur than sulphocyanogen, and yet capable of reddening persalts of iron like a sulphocyanide: for even when the stage of slow decomposition of permanganate commences, the addition of perchloride of iron produces intense reddening; and if we may make a supposition from the amount of oxygen contained in the permanganate which has been used up to this point, namely 3 atoms of oxygen for 1 at. of sul-

phocyanide, which would suffice to oxidise half the sulphur, the body remaining should have the composition HSCy. Gay Lussac did, indeed, in 1815, prepare a body by the direct combination of cyanogen and sulphuretted hydrogen, to which Laurent assigns the above composition, though others have declared it to be a *sesqui*-hydrosulphate of cyanogen. Should Laurent's formula be correct, it appears by no means unlikely that it may be the intermediate body which is wanted to explain the fact—of there being at least two stages in the decomposition of sulphocyanides by permanganate of potash; it is, however, described as so unstable, and the properties assigned to its solution are so little characteristic, that no attempt has been made to prove their identity.

This method of liberating hydrocyanic acid from sulphocyanides, namely, by oxidation in the moist way, may perhaps be profitably applied by some gas companies to the production of ferrocyanides from the hitherto useless sulphocyanides contained so abundantly in the waste materials after their employment for gas purification. In the case of gas-lime, the quantity of hyposulphites likewise present, would most probably prevent its profitable application, but this is not the case with waste hydrated oxide of iron; here no hyposulphites are present to interfere, and the sulphocyanide (chiefly of ammonium,) is likewise contained in a much more concentrated form, and is extracted by water without the least difficulty, so that its employment for such a purpose is in every way the best. The two requisites are of course a cheap source of oxygen, and a ready mode of separating the hydrocyanic acid for conversion into ferrocyanide. Peroxide of manganese with sulphuric acid at first suggested itself as a cheap oxidizing material likely to answer, and various experiments were made to determine how nearly the product obtained corresponded with what theory required. Distillation was the method employed for the separation of the hydrocyanic acid, which it effects very rapidly and easily. It was found, however, that only about $\frac{3}{4}$ of the whole amount of hydrocyanic acid was actually obtained, and if the mixture was too concentrated, or too much sulphuric acid had been used, considerably greater loss of hydrocyanic acid was sustained, due to its partial conversion into formic acid and ammonia.

Nitric acid was then tried, and found to be a much more satisfactory means of oxidation; the decomposition is much more complete, simple, and rapid; the nitric acid is little, if at all, destructive to hydrocyanic acid, so that from 80 to 90 per cent. of

the theoretical amount is readily obtained; and, on one occasion, when especial care had been taken in the condensation, the entire theoretical amount of hydrocyanic acid was collected. Again, nitric acid being fluid, it mixes with the sulphocyanide, and thus presents no obstacle to distillation in a still such as Coffee's, contrived to admit of the continuous distillation of a flowing stream, exposing a large surface for evaporation, which would be a more difficult matter if any insoluble oxidizing agent were employed. The hydrocyanic acid thus obtained is readily condensed, by allowing the products of distillation to pass into an alkali, or a milk of some alkaline earth—and the cyanide produced is afterwards readily convertible into ferrocyanide, by adding to the alkaline solution a proto-salt of iron as long as the protoxide at first precipitated is redissolved by stirring or the green colour of the mixed oxides changes to red. Milk of lime might be used to absorb the hydrocyanic acid, which could then be converted into ferrocyanide of calcium by protochloride of iron, and separated by crystallisation from the other salts present; and the calcium salt might afterwards be converted into the corresponding potassium salt by carbonate of potash. Were the nitric acid in its action on sulphocyanides readily to part with 3 atoms of oxygen becoming reduced to NO_2 , nothing could be more satisfactory; for the deutoxide separated from the hydrocyanic acid by means of the base, might afterwards be brought in contact with the oxygen of the air, and thus be again rendered fit for employment for the same purpose; unfortunately, however, the deoxidation of the nitric acid does not, for the most part proceed further than the reduction of it to NO_3 , which is consequently taken up by the lime or other base, together with the hydrocyanic acid; this does not, however, prevent the conversion of the cyanide of calcium, &c. into ferrocyanide, provided the base employed be in excess. The nitrite of lime in the mother liquid, after the crystallising out of the ferrocyanide, though not readily available for oxidising a fresh quantity of sulphocyanide, might yet be advantageously employed in the manufacture of sulphuric acid from the sulphur likewise so abundantly contained in gas refuse, for the weakest acid suffices to evolve the nitrous acid, even in the cold.

II. The action of nitric acid on sulphocyanides is attended with a reaction, which scarcely seems to have been noticed in any chemical work, namely, that, just as the action commences, an intense reddening of the liquid occurs, most closely resembling in

colour a solution of sulphocyanide of iron. When first observed, I did not feel satisfied that, because no iron could be detected in the mixture by ordinary tests, there was none really present, for, on the one hand, sulphocyanide of potassium *might* exceed all other tests in delicacy, or, on the other, some cyanogen compound of iron might be present, in which the properties of the metal were disguised until liberated by the action of nitric acid; that such, however, was not the case, was ascertained by boiling the red liquid until it had become colourless from the destruction of the sulphocyanides, and when cool, adding more of the sulphocyanide. Had the tint been due to iron, the red colour would then have been restored, as it was, however, it remained colourless. Pure colourless nitric acid produces no colour when added to a sulphocyanide in the cold; if, however, the temperature be slightly raised, coloration takes place immediately, attended with simultaneous formation of sulphuric acid; for if a little chloride of barium be previously added, a cloud of sulphate of baryta will be seen to make its appearance, together with the first shade of red. If, however, red nitrous vapours be passed into a sulphocyanide, the same intense colour is produced, but without the immediate formation of sulphuric acid, although this soon takes place; and if chloride of barium be added, it may be observed, that when the cloud of sulphate baryta begins to appear, the liquid at the same time begins to lose colour. Pure nitrous acid, as evolved from a nitrite, on treating it with acetic acid, has no power of colouring a sulphocyanide; for when a solution of the latter is added to a mixture of the two former, no change is observed, even though the atmosphere above the liquid is coloured. The acetic acid in no way prevents the coloration by nitrous vapours, whether evolved from nitric acid acting on starch, or obtained by the oxidation of binoxide of nitrogen; hence it appears that peroxide of nitrogen is really the agent which produces the coloration of a sulphocyanide. Having ascertained that a sulphocyanide was coloured by peroxide of nitrogen, but not by nitrous acid, I hoped by its means to ascertain whether the so-called hyponitrate of lead, obtained by boiling the nitrate with metallic lead, were really a direct compound of oxide of lead and peroxide of nitrogen, or not rather a mixture of basic nitrite and nitrate of lead, concluding that if NO_3 (an acid,) were displaceable by acetic acid, NO_4 , being, as its name would lead us to infer, an oxide, and even stated to have no acid properties, would at least be equally readily liberated

by acetic acid; on making the experiment with various basic nitrites and hyponitrites of lead, no trace of NO_4 could be detected. These experiments, however, in reality entirely fail to settle the point; for NO_4 , though termed an oxide, behaves, in all cases, like a combination of NO_5 and NO_3 , so that if the gases which powerfully redden sulphocyanide be first passed into an alkaline solution, and the product be then treated with acetic acid and a sulphocyanide, no reddening occurs, although vapours of NO_3 appear abundantly, showing that the base has split the NO_4 into NO_5 and NO_3 ; the same is the case when NO_4 is passed into an alkaline acetate; here, however, NO_5 only is absorbed and NO_3 remains free, and thus we have a method of freeing NO_3 from NO_4 . The point, however, to be noticed is, that acetate of lead acts in the same way, decomposing NO_4 into NO_5 , which is absorbed, and NO_3 , which escapes; hence it is evident, that even if the lead-compound really contained NO_4 , the latter, liberated in presence of the acetate of lead then formed, would be instantly decomposed as above stated. When the product obtained by passing NO_4 into an alkaline solution, is supersaturated with an acid stronger than acetic, and then tested with a sulphocyanide, the deep red is again obtained, which it might be imagined was due to the simultaneous liberation of the NO_5 and NO_3 , and their union to form the NO_4 from which they were produced; neither is it a conclusive argument against this view, that the acids employed were too dilute to liberate nitric acid perceptibly from pure nitrates, for in the former case the additional affinity of NO_3 for NO_5 would come into play. It was found, however, that nitrites, however carefully prepared, by double decomposition from pure nitrite of silver, or by extraction from crude nitrites with alcohol, always acted in the same manner when treated with a stronger acid, hence it appeared probable that NO_3 really produces the reaction with *free* hydrosulphocyanic acid, though not with a sulphocyanide, and that the reason why a mixture of a sulphocyanide and nitrite remained colourless when treated with acetic acid, was that the latter was a weaker acid than hydrosulphocyanic acid, and not being capable of liberating it, the coloration with NO_3 could not occur; and this was found to be the case, for on preparing pure HS_2Cy and exposing it together with a sulphocyanide to the vapour evolved from a nitrite and acetic acid, the former was instantly reddened, while the latter remained colourless, and on adding to the reddened HS_2Cy a solution of any acetate the colour disap-

peared, in consequence of the HS_2Cy entering into combination with the base in preference to the acetic acid, and being thus rendered incapable of reacting with NO_3 . The action of NO_4 on salts with weak acids explains also its behaviour with sulphocyanides; for here as in other cases, we may conclude that it is split into NO_5 and NO_3 , the former liberating HS_2Cy , which is then in a condition to be coloured by the latter. Hence, although sulphocyanides serve as a test to distinguish between NO_4 and NO_3 in a gaseous mixture, it appears that the colour produced is really due to the mutual presence of *free* NO_3 and *free* HS_2Cy . The colour does not appear to be due to any decomposition of the HS_2Cy , for in consequence of the large amount of HCy obtainable by the action of nitric acid on sulphocyanides (which seems to show that the whole action is expended on the sulphur) we must conclude that the very first symptom of decomposition will be the appearance of sulphuric acid, for such is the case when a mixture of a sulphocyanide, chloride of barium, and nitric acid, are gently heated, the instant a reddish tint appears, showing that the nitric acid has undergone reduction and parted with some oxygen, a cloud of sulphate of baryta also appears. This is not the case, however, immediately when NO_4 is passed into the mixed solutions of a sulphocyanide and a baryta salt, the red colour remains some little time before a cloud appears, and substances capable of combining with NO_3 such as bases or even alcohol immediately decolorise the mixture, the latter thus furnishes an additional means of distinguishing between the colour due to oxides of nitrogen and that due to persalts of iron. The combination, therefore, which produces the red colour seems to be similar in the feebleness of its character to that of the black compounds which ferrous salts form with NO_2 , which are stated to be destroyed by simply placing in a vacuum.

In conclusion it may be observed that the fact of a *portion* of the sulphur in protein compounds being more difficult of detection than the remainder—taken into consideration with the appearance of hydrocyanic acid amongst the products obtained by the action of oxidising agents on albumen, &c.,—seems to suggest the possibility that this latent condition of the sulphur may be due to its union with the hydrocyanic acid as sulphocyanide, perhaps further combined with the alcohol-radicals corresponding to those acids which likewise appear amongst the products of oxidation of protein bodies. The fact of the existence of sulphocyanides in the body seems to show that such an explanation is not utterly improbable.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

Anniversary Meeting,—March 30, 1858.

Dr. Lyon Playfair, C.B., President, in the Chair.

The Report of the Council, and the audited account of the Treasurer, were read as follows:—

REPORT OF THE PRESIDENT AND COUNCIL.

THE late President of the Society, at the last Anniversary, explained the arrangements then in progress for giving to the Chemical Society adequate accommodation in Burlington House. Since that time, the Society has taken possession of the rooms in that house placed at its disposal by the Government, under a common arrangement with the Royal and Linnæan Societies. The expense of removal from the former rooms in Cavendish-square and the cost of fittings in the present apartments, have not entailed a charge upon the funds of the Society, having been met by a voluntary subscription of the Fellows. The day of meeting was changed from Monday to Thursday, in order that the Chemical Society might meet on the same days as the Royal and Linnæan Societies. The advantage of this change has been obvious, not only to the Fellows of our own, but also to those of the other two Societies, their meeting-rooms having been made readily accessible to all who felt interested in any particular paper which might be read in either of the Societies in question.

During the last year, 39 Fellows have been elected, a number greater than that in any year since the one subsequent to the formation of the Society in 1841. But the increase in the Society has not been proportional to the elections, for it has been found

necessary to remove 15 Fellows from the list, on account of default in the payment of their subscriptions. The present number in the Society is as follows :—

Number of Fellows on 30th March, 1857	269
Fellows admitted since that date	30
Do. resigned	2
Do. deceased	5
Do. removed in default of subscription .	15
	<hr/>
Increase	8
	<hr/>
Present number of Fellows	277
	<hr/>

On the last Anniversary, the number of our Associates was 14, of whom two have been elected Fellows; only one has been since elected, so that the present number of Associates is 13. On the 30th of March last, our Foreign Members numbered 23, of whom one is now deceased; and two, namely, Auguste Cahours and C. A. Lehmann, have been elected.

The deceased Foreign Member, Baron Thénard, is a name long known with honour to all chemists. He was born on the 4th of May 1777, at Nogent-sur-Seine, in Champagne. His father was a poor farmer, who made many sacrifices to educate his son. Young Thénard, after having had a liberal education at an academy in Sens, went to Paris, when 16 years of age, with the view of studying Pharmacy, in order that he might return to Champagne. In the laboratory of Vauquelin, he first acquired his strong taste for Chemistry, and to that chemist is due the foundation of Thénard's fortunes. Through Vauquelin's influence, he obtained an appointment in the Ecole Polytechnique, and attracted the attention of many chemists, among others of Gay Lussac, Berthollet, and Laplace, by the skill and dramatic powers of his lectures. In 1800, being now 23 years of age, he published his first memoir, being one upon the compounds of Antimony and Oxygen. The Institute gave to this paper high encouragement, and in the following year Thénard presented another memoir on Sebacic Acid, showing that it might be obtained by distilling various fatty substances. In the following year, Vauquelin resigned the chair of Chemistry at the Collège de France, and recom-

mended that his former pupil should be his successor. He was now raised to a professorship in the Ecole Polytechnique, and, in 1807, associated himself with Gay Lussac in prosecuting that brilliant series of discoveries in Chemical Physics for which their names are so justly celebrated. Among these were described two modes of analysing organic substances, and a great impulse was thus given to a new and most important department of Chemistry. In 1810, Thénard was elected to succeed Fourcroy as a member of the Institute, and had a third professorship bestowed upon him at the Faculté des Sciences de Paris. His power and popularity as a teacher seemed to remain undiminished by this heavy addition to his labours, and for 20 years he continued head lecturer to audiences of more than a thousand persons.

In 1812, he published his *Traité Élémentaire de Chimie Théorique et Pratique*, a work which acquired a European reputation, and did much to diffuse a knowledge of Chemistry by the masterly and clear manner of its exposition.

In 1818, he made his remarkable discovery of peroxide of hydrogen, and afterwards of various other oxides, particularly of calcium and strontium. Some of these are probably compounds of the metallic protoxide with peroxide of hydrogen.

In 1827, he entered the Chamber of Deputies as a Moderate Liberal; and, after the Revolution of 1830, was called, with his friend Gay Lussac, to the House of Peers.

He now took a leading part in public matters connected with the progress of science and literature, and contributed much to the growth of scientific schools and institutions in France.

Even during the last year of his active life, he continued the study of chemistry, in a joint research with his son Paul Thénard; and died, after a short illness, on the 21st of June last.

Death has removed from our Society two of its original members. One of them was Mr. Brooke, the distinguished crystallographer. Henry James Brooke was born at Exeter on the 25th of May, 1771. He first studied for the bar, but subsequently went into the woollen trade, as his relatives were actively engaged in the manufacture of broad cloth. In the prosecution of this business he lived for two years in Spain, and took up his residence in London in 1802. He had already shown a decided taste for Mineralogy, Geology, and Botany, and continued to study them with ardour when his industrial pursuits gave him leisure. After some fluctuations in his commercial pursuits, he attached himself

to a Life Assurance Association as its secretary, having long shown an interest in the questions involved in Life Assurances.

In 1823, he published his "Familiar Introduction to Crystallography," and much simplified and improved this treatise in the *Encyclopædia Metropolitana*.

Mr. Brooke recognised at an early period the use of the reflective goniometer for the measurement of laboratory crystals, of which he examined a large number of specimens.

Up to within a short period of his death, which took place on the 27th of June last, he continued to occupy himself with his favourite science.

Professor Edmund Davy, another of our original members, died on the 5th of last November. He was born at Penzance in 1785, where he remained until his cousin, Sir Humphrey Davy, appointed him to the office of an assistant in the laboratory of the Royal Institution, in 1804. The eight years during which he occupied this post were very fruitful in chemical discovery, and Mr. Davy had the advantage of acquiring a large and varied experience. In 1813, he was appointed Professor of Chemistry to the Royal Institution of Cork, where he remained for 13 years; after which he was appointed to a similar chair in the Royal Dublin Society, as a successor to Mr. Higgins, well known for his views on the Atomic Theory. In both these chairs, Professor Davy laboured zealously to make known the discoveries of chemical science by courses of lectures, marked for their clearness of exposition and for the care of their preparation.

Professor Davy published many memoirs on chemical subjects in the scientific journals; those upon new compounds of Platinum, on the Fulminates, and on a new Hydrocarbon, being among the more conspicuous. He continued at work in his laboratory until within a few months of his death. In him, the Royal Dublin Society has lost a teacher long and favourably known in connection with that Institution, not only from his professional labours, but also for his great moral worth and warm disposition.

Papers read at the Meetings of the Chemical Society, between March 30, 1857, and March 30, 1858:—

"On a New Base obtained from the Juice of Flesh:" by Professor Strecker.

"On the Juice of Beef:" by Professor Bloxam.

- "On a New Method of Testing Urine:" by Mr. J. Horsley.
- "On the Fatty Matters of Human Excrements in Disease:" by Dr. Marcet.
- "On some Products of the Oxidation of Chinese Wax:" by G. B. Buckton, F.L.S.
- "On the Chemical Changes which Pig Iron undergoes during its Conversion into Wrought Iron:" by Messrs. F. Crace Calvert and R. Johnson.
- "On a New Series of Organo-thionic Acids:" by J. T. Hobson, Ph.D.
- "Notice of a New Maximum and Minimum Thermometer:" by Rev. J. G. Macvicar.
- "On an Optical Test for Didymium:" by Dr. J. H. Gladstone, F.R.S.
- "Some Chemical Facts respecting the Atmosphere of Dwelling Houses:" by Dr. H. E. Roscoe.
- "Remarks on the Action of Heat on Gold, and its Alloy with Copper:" by Mr. James Napier.
- "Contributions towards the History of Thialdine:" by Dr. Hofmann.
- "Analysis of the Water of Tunbridge Wells:" by Mr. John Thomson.
- "On the Action of Sulphuric Acid on Anisic Acid:" by M. Louis Zervas.
- "On the Separation of Iodine, Bromine, and Chlorine, and the comparative degree of Affinity of these Elements for Silver; with some Analyses of their combinations with that Metal occurring in Chili:" by Mr. Frederick Field.
- "On some Constituents of Rhubarb:" by Dr. Warren De la Rue, and Dr. Hugo Müller.
- "On the Volumetrical Determination of the Carbonic Acid in the Air:" by Professor Pettenkofer.
- "On a New Calotype Process:" by Mr. J. Mercer.
- "On Rosolic Acid:" by Dr. Hugo Müller.
- "On the Arseniates of Baryta, Lime, and Magnesia, and the separation of Arsenic from other elements:" by Mr. F. Field.
- "On the existence of a second Crystalline Fluorescent Substance, Paviine, in the Bark of the Horse-chestnut Tree:" by Professor Stokes, Sec. R.S.
- "On a New Maximum and Minimum Mercurial Thermometer:" by the Rev. Dr. Macvicar.

- “On the Chemical Action of Water on Soluble Salts:” by Dr. J. H. Gladstone, F.R.S.
- “On Poly-atomic Ammonias:” by Dr. Hofmann.
- “On the Iodo-sulphates of the Cinchona Alkaloids:” by Dr. W. Bird Herapath.
- “On the Action of Bromine on Acetic Acid:” by Messrs. Perkin and Duppa.
- “On a Poison obtained from Arrows:” by Mr. Henry Hancock.

Discourses delivered since March 30, 1858.

- “On the Applications of Sewage to Agriculture:” by Mr. Dugald Campbell.
- “On the Alkaline Products of the Destructive Distillation of Animal Matter:” by Dr. Thomas Anderson, F.R.S.
- “On the Recent Progress of Electro-Chemistry:” by Dr. W. A. Miller, F.R.S.

Messrs. Dugald Campbell and George Maule having been appointed Scrutators, the meeting proceeded to the election of Council and Officers for the ensuing year, and the following were declared to have been duly elected:—

President.—Dr. Lyon Playfair, C.B., F.R.S.

Vice-Presidents who have filled the office of President.—W. T. Brande, F.R.S.; Dr. C. G. B. Daubeny, F.R.S.; Thomas Graham, F.R.S.; Dr. W. A. Miller, F.R.S.; Col. Philip Yorke, F.R.S.

Vice-Presidents.—B. C. Brodie, F.R.S.; Dr. H. B. Jones, F.R.S.; Robert Porrett, F.R.S.; Dr. John Stenhouse, F.R.S.

Secretaries.—Theophilus Redwood, Ph.D.; W. Odling, M.B.

Foreign Secretary.—Dr. A. W. Hofmann, F.R.S.

Other Members of Council.—F. A. Abel; G. B. Buckton F.R.S.; Dr. E. Frankland, F.R.S.; Dr. J. H. Gilbert; Dr. W. C. Henry, F.R.S.; Dr. G. D. Longstaff; Nevil Story Maskelyne; John Mercer, F.R.S.; Dr. H. M. Noad, F.R.S.; Alfred Smee, F.R.S.; Dr. J. A. Voelcker; Dr. A. W. Williamson, F.R.S.

The following resolutions were passed :—

1. That an alteration be made in the seventh paragraph of the first bye-law, in the fourth and fifth lines of the paragraph, to the effect, that the words “ be calculated from the Ladyday or Michaelmas preceding their election ” be struck out, and the words “ become due on the first day of January in each year, ” substituted for them.

2. That a list of the names of those gentlemen who have not paid the subscriptions due from them at the present time, be suspended in the library and meeting-room.

3. That the thanks of the meeting be given to the President, Officers, and Council, for their services during the past year.

4. That the thanks of the Society be given to Professor Graham, and the other gentlemen who subscribed towards the removal fund, whereby the removal was effected without any drain upon the ordinary funds of the Society.

5. That the thanks of the meeting be given to the Auditors for their kindness in examining the accounts.

April 1, 1858.

Dr. Lyon Playfair, C.B., President, in the Chair.

Henry Davis Pochin, Esq., Chemical Manufacturer, Manchester, and Richard Taylor, Esq., Charlbury, Oxfordshire, were elected Fellows of the Society.

The following papers were read :—

“ On a new method of preparing Propionic Acid, ” by Mr. J. A. Wanklyn.

“On some compounds of Iodide and Bromide of Mercury with the Alkaloids,” by Mr. T. B. Groves.

April 15, 1858.

Dr. Lyon Playfair, C.B., President, in the Chair.

J. Thomson, Esq., Royal College of Chemistry,
T. Thomas, Esq., 2, Redland Parade, Bristol, and
J. Hindle, Esq., Sabden, near Whalley, Lancashire,
were elected Fellows of the Society.

Dr. Odling delivered a discourse “On Atoms and Equivalents.”

May 6, 1858.

Dr. W. A. Miller, Vice-President, in the chair.

The following donations were announced :—

“The Pharmaceutical Journal,” from the Editor.

“The Journal of the Society of Arts,” from the Society.

“Abel and Bloxam’s Handbook of Chemistry,” second edition,
from the Authors.

“Annales des Sciences Naturelles.”

The following were elected Fellows of the Society :—

Edward Davies, Esq., Royal Institution, Manchester.

Siméon Stoikowitsch, Esq., Royal Institution, Manchester.

Alfred Binyon, Esq., Mayfield Print Works, Manchester.

Charles O’Neil, Esq., Manchester.

Richard Johnson, Esq., Dale Street, Manchester, and

Thomas Toase, Esq., Wesleyan College, Hayti.

Dr. Martin Von Bose, of Cary Street, was elected an Associate of the Society.

Dr. Odling continued his discourse “On Atoms and Equivalents.”

May 20, 1858.

Dr. Lyon Playfair, C.B., President, in the Chair.

George Parry, Esq., Ebbw Vale, Newport, Monmouthshire,

and William Charles Paterson, Esq., Ashville, Partick Hill, Glasgow, were elected Fellows of the Society.

Dr. Angus Smith delivered a discourse "On the Air of Towns."

June 3, 1858.

Dr. Lyon Playfair, C.B., President, in the Chair.

Messrs. Mark Lansdell and John Collis were elected Associates of the Society.

The following papers were read:—

"On the quantitative estimation of Sulphides, Sulphites, Hypo-sulphites, and Sulphates, in the presence of one another," by Mr. J. W. Kynaston.

"On the Composition and Analysis of Black Ash or Ball Soda," by the same.

"On Nitrite of Amyl and its Derivatives," by Dr. F. Guthrie.

"On a new method of preparing Peroxide of Chlorine," by Messrs. Crace Calvert and E. Davies.

"On the Deposits found in the Chimneys of Gold and Silver Reverberatory Furnaces," by Mr. J. Napier.

"On the formation of Chrysammic Acid by the action of Nitric Acid on Aporetin," by Drs. Warren De la Rue and Hugo Müller.

June 17, 1858.

Dr. Lyon Playfair, President, in the Chair.

Dr. Edward T. Kirkpatrick, 12, Park Lane,

Dr. Bond, B.A., M.B., Queen's College, Birmingham, and

John Williams, Esq., 5, Old Cavendish Street, were elected Fellows of the Society.

A resolution of the Council was read, recommending that the names of six Fellows, whose subscriptions are in arrear, be removed from the List of Fellows of the Chemical Society.

Dr. Hofmann delivered a discourse "On Ammonia."

The titles of the following papers were read:—

"On the general action of oxidising agents on Sulphocyanides,

and on a special reaction attending the use of Nitric Acid," by Mr. E. A. Hadow.

“Mineralogical Contributions, containing communications:—

“On Meteoric Iron from Zacatías in Mexico,

“On Pseudomorphous Cinnabar, from Spain,

“On Libethenite, from Southern Africa,

“On Columbite, from Greenland,” by Dr. Hugo Müller.

“On the amount of, and the relation between, the chief constituents of the Food Grains of India,” by Dr. Forbes Watson.

1857.	1858.	£	s.	d.
April 1.	March 26.	139	4	4
May 14.	"	7	10	0
Oct. 22.	"	15	0	0
Dec. 5.	"	15	0	0
" 19.	"	100	0	0
1858.	"	0	2	0
Feb. 8.	"	6	15	0
March 4.	"	80	0	0
"	"	60	0	0
"	"	14	0	0
"	"	23	0	0
"	"	72	0	0
"	"	55	19	0
"	"	152	0	0
"	"	50	0	0
		790	10	4
		£	s.	d.
To Balance received from Mr. Porrett		401	12	4½
" Rent from College of Dentists to 25th		150	0	0
" March, 1857				
" Rent from College of Dentists to 29th Sep-				
" tember, 1857				
" Rent from Meteorological Society				
" Fixtures of Old Apartments				
" Sale of Memoirs, part 4				
" Three half-yearly Dividends on £150 Stock				
" Sundry Receipts from 1st April, 1857, to				
" 26th March, 1858, as below :—				
Life Compositions				
Admission Fees				
" Subscriptions due previous to 1857 :—				
Resident Members				
Non-resident do.				
" Subscriptions for 1857 :—				
Resident Members				
Non-resident do.				
" Subscriptions for 1858 :—				
Resident Members				
Non-resident do.				
		£	s.	d.
Balance brought down		401	12	4½
3 per Cent. Consols		150	0	0
		£551	12	4½
		£	s.	d.
By Sundry Payments, as under :—				
Rent of Apartments in Cavendish-square to				
Michaelmas, 1857		60	0	0
Attendance		5	0	0
Gate Porter of Burlington House		1	1	0
Refreshments		8	12	10
Gas		2	5	6
Repairs		0	6	6
Magazines		7	0	0
Carriage of Books		0	19	6
Printing Journal		117	6	1
Binding account, 1855 to 1856 inclusive ..		41	12	3
Librarian's Salary		15	0	0
Editor of Journal's Salary (three-quarters		37	10	0
of a year)		2	0	0
Clerk		25	2	6
Collector's Commission and Expenses		1	1	0
Subscription to Cavendish Society		1	1	6
Law.—Power of Attorney to Treasurer ..		1	10	0
Translating Foreign Papers		2	3	0
Engraving Certificate of Foreign Membership		18	18	0
Removal Fund		9	5	6
Printing		5	17	2
Stamps, Stationery, and Postages		20	0	0
Proceedings of Royal Society		4	5	7½
Petty Expenses		387	17	11½
By Balance :—		401	18	0
At Courts and Co.		0	14	4½
Cash		790	10	4
		£	s.	d.

ASSETS.
 Balance brought down 401 12 4½
 3 per Cent. Consols 150 0 0
 £551 12 4½

Examined and found correct,
 JOHN BARLOW,
 W. MARCET,
 ALFRED E. FLETCHER, } *Auditors.*
 London, 29th March, 1858.



THE
QUARTERLY JOURNAL
OF
THE CHEMICAL SOCIETY.

XVII.—*On a new method of preparing Hypochloric Acid or Peroxide of Chlorine.*

BY F. CRACE CALVERT, F.C.S., AND E. DAVIES, F.C.S.

WE were recently led to study the action of chlorate of potash on oxalic acid, and found that when these two bodies were heated together, a yellow gas was produced, the composition of which we have studied. We think that it will be interesting to the Chemical Society to know that this substance, which has hitherto been so dangerous to prepare, on account of the violent action which sulphuric acid produces on chlorate of potash, can now be obtained without the slightest risk, by using the process and taking the precautions which we shall describe. Even when a large quantity of chlorate of potash is used relatively to the quantity of oxalic acid, no violent action ensues, unless a very strong heat is applied, when a deflagration takes place and the flask is generally broken; whilst, by employing excess of oxalic acid, regulating the temperature as described, and stopping the operation when ClO_4 ceases to be disengaged, no accident can happen, and this gas may be exhibited at a lecture, or prepared for any other purpose with as much facility as any other compound of chlorine and oxygen.

The gas was prepared by heating in an oil or water-bath to about $70^\circ\text{C}.$ ($158^\circ\text{F}.$), pure and well pulverized chlorate of potash and crystallized oxalic acid, when the gas is steadily

given off accompanied by carbonic acid; when action ceases, raising the temperature above 70°C . does not cause a further evolution of hypochloric acid, as above this temperature the gas is decomposed and a mixture of chlorine and oxygen given off. We found that the addition of water to the materials diminished the amount of hypochloric acid produced.

It would appear at first probable that the reaction should consist in one equivalent of chlorate of potash oxidizing one equivalent of oxalic acid, and producing hypochloric acid, carbonic acid, and carbonate of potash; but we have not been able to effect this, as with these proportions, large quantities of both chlorate of potash and oxalic acid escape decomposition. We therefore increased the quantity of oxalic acid to 2, 3, 4 and 5 equivalents, but still could not entirely drive off all the chlorine of the chlorate of potash combined as ClO_4 , though the quantity produced increased in the ratio of the additional number of equivalents of oxalic acid. This result is not due to want of intimate mixture, as towards the end of the operation the mixture becomes semi-fused, and also on repeating the experiment with the same quantities of materials, a constant quantity of ClO_4 was always obtained. As with six equivalents of oxalic acid, $\frac{2}{3}$ of the chlorine contained in the chlorate of potash employed was given off as ClO_4 , we tried an experiment, using 9 equivalents, and found that $\frac{5}{6}$ of the chlorine of the chlorate of potash was given off as ClO_4 , the remaining $\frac{1}{6}$ being in the residue in the flask as chloride of potassium. The latter proportions are those with which we have prepared the gas for various experiments.

From these results it appears probable that the formation of the ClO_4 is due to the liberation of the chloric acid, by formation of an acid oxalate of potash, the free chloric acid being afterwards decomposed by the excess of oxalic acid.

After several experiments, we found that the following process for analysing the gas gave the best results. A saturated aqueous solution of the gas being prepared, a stream of sulphurous acid was passed into the liquor until it was decolorised.

The liquid now containing sulphuric and hydrochloric acids was divided into four equal portions, and in two of these the sulphuric acid was determined as sulphate of baryta by boiling to expel excess of sulphurous acid and precipitating with chloride of barium. In the other two portions, the hydrochloric acid was determined as chloride of silver. From the weights thus obtained it was easy

to calculate the formula of the gas; for, as one equivalent of chlorine would cause the oxidation of one equivalent of sulphurous acid, and as each equivalent of oxygen in the compound had a similar effect, each equivalent of chlorine should correspond to as many equivalents of sulphuric acid as there were equivalents of chlorine and oxygen together in the compound.

Thus, if the compound were ClO_4 , there should be for each equivalent of chlorine 5 equivalents of sulphurous acid oxidized into sulphuric acid. The following figures will show how closely the results obtained coincide with those calculated from the formula.

Chloride of Silver found.	grms.	Sulphate of Baryta found.	grms.	Sulphate of Baryta calculated supposing the compound to be ClO_4 .
				grms.
No. 1	·192		·776	·780
No. 2	·221		·882	·865
No. 3	·235		·955	·955

In order that there may be no doubt as to the above being the composition of the gas, we give the quantity of sulphate of baryta which should be produced if its formula were ClO_3 .

Sulphate of Baryta found.	grms.	Sulphate of Baryta calculated supposing the compound to be ClO_3 .
		grms.
No. 1	·776	·620
No. 2	·882	·705
No. 3	·955	·764

From the simplicity and accuracy of the above process, we think that it may be applied to the analysis of other compounds of chlorine and oxygen.

We have endeavoured to decide the question as to whether this substance possessed acid properties or not, but could not do so, as by this method of preparation, the hypochloric acid is accompanied by a large quantity of carbonic acid, which interferes with any attempt to combine it with bases.

The powerful oxidizing action of this gas, containing as it does both chlorine and oxygen, will probably render it a valuable agent in organic chemistry, now that it can be easily prepared.

We have also been examining the compound of chlorine which is formed in making oxygen from chlorate of potash and peroxide of manganese, and find that it is probably chlorous acid, ClO_3 . We cannot, however, speak positively on this point, owing to the

very small quantity which is produced. By using perfectly pure materials the oxygen is free from this compound, the quantity of which increases with the impurities of the chlorate of potash and peroxide of manganese, especially the latter. It is also more abundant when the oxygen is produced rapidly. The white fumes often perceived in oxygen rapidly prepared are composed of volatilized chloride of potassium.

XVIII.—*On the Air of Towns.**

BY DR. R. ANGUS SMITH.

It is now a long time since I first sent a short paper on this subject to the Chemical Society, showing that the existence of organic matter in the air capable of decomposing and actually undergoing decomposition was not a matter of theory but of reality. At a later time I was able to confirm the fact, but a mode of readily ascertaining it in all degrees of amount has always been a great desideratum, a problem for pure science as well as for science in its relations to the welfare of man; this latter department is one which will always be most interesting to the greater number, and one which receives a constant impulse from the great amount of sickness existing in the world. I wish now to give some further particulars of the principal points which I have been able to ascertain. One or two of these have been subjects of professional inquiry, *i.e.*, made to serve a purpose connected with the interests of individuals or corporations or the demands of the law, but the greater portion and that of most importance has been gradually accumulated; and whilst making this observation I think it well to add that it seems to me a most unfortunate oversight that whilst laws have been made with relation to the impurity of the atmosphere arising from many causes, neither those who made the laws nor those who administer them have ever taken pains to find out what it really was against which they combated, and what crime that was which they have been so anxious to punish. The same carelessness has been observ-

* This was written in such a manner as to enable me to compress the material into the usual size of a lecture; it will be found that many parts appear more like notes or fragments. On the more important points, such as the estimation of organic matter, it will be necessary to give a second paper, for which there is already material collected.

able on the side of those towards whom the law acted, and decisions have in reality been in the hands of those whose fancy or caprice have led them to take advantage of legal enactments; whilst great offenders have frequently escaped because no one has known the points on which they could be most easily assailed. The impurities of an atmosphere have been rudely guessed at and the actual sources have been found only in a general manner; when particular cases have demanded attention, there has been great difficulty in arriving at well defined conclusions. As to any attempt to measure the degree of impurity in the air, none has been made to my knowledge, unless we take that gauge to be the true one which, in the registrar-general's returns, presents us with a result where each percentage stands for nearly 300,000 human lives.

If science can define precisely the extent of the evils which so affect human life, it may at a second stage also attain the important desideratum of a cure, and at any rate any inquiry of the kind must be of interest to all, but especially so to the medical and chemical professions.

In studying the air of towns in which coals are burnt, no place can give such an opportunity as Manchester, being the largest manufacturing town of the world, and itself being the centre of a great manufacturing district. Geographically, it is not the centre, being near the outskirts of the district on the south-west side, whilst on every other side manufactures extend for, perhaps, on an average thirty miles. They extend from the south and south-east on the borders of Cheshire and Derbyshire onwards to Preston on the north, Liverpool on the west, and into Yorkshire on the east; and within this district are large towns, little known to fame, but containing a great working population, having, besides wealth, both intelligence and force. In this district, comprehending many hundred square miles, there is every variety of scenery, but I believe every portion of it may be shown to be influenced by the smoke of the workshops. The tinge of darkness in the atmosphere may be seen making a line of at least forty miles in length, and affecting the appearance of the sky and the landscape. At the same time, it is marvellous how rapidly nature asserts her superiority in all this accumulation made by art. The moment we leave a town we see every thing greener and fresher, and the people larger, broader, happier and cleaner; and so much so is this the case, that in the great district of which I have spoken,

there is no doubt in the minds of those who are only a little removed from towns, that they are breathing the purest air. Nor is it without difficulty that we can perceive that the towns to some extent affect the whole district. The eye becomes accustomed to the stunted trees and the many withered branches, and broken-up hedge-rows; nor is it customary to look at the state of the individual leaves to enquire how far degeneracy has advanced. The eye is sufficiently pleased to see the general aspect of pure green which refreshes us in every portion of the district, for the meadows in spring and summer seldom seem to suffer, but rather to be improved, partly by direct and partly by indirect assistance from the towns.

In some places, however, the destruction may be called total, the trees that exist being either absolutely dead or only capable of showing a very feeble life; and this it seems to me is very much the case in proportion to their height, although certain of them, such as the poplar, even if less tall, suffer on account of a greater delicacy. The smoke may either rise or fall or move horizontally. It rises when the barometer is high, the air dry, and the sky clear, at which time we perceive very little of the effects on the ground; it falls when the clouds are low, or the air laden with moisture; then the whole district is equally enveloped in the haze. In general there is a movement of the air and a motion of the smoke in a direction more or less horizontal, from the top of the chimney. By this means the highest objects are first attacked and the trees decay from the summit or from the upper part of that side exposed to the current. They resist the enemy for many years, keeping for a long time at least one side fresh; even the owners do not for years perceive that the district is gradually becoming unfit for plants of great height, but as they lose some favourite flower or shrub, they pitch on some person most easily attacked and blame him for all the mischief.

About St. Helens there are many miles of trees broken, stunted, and rotten, and between all the towns of Lancashire, according to the prevailing sweep of the wind, there are lines of dead hedges. Yet the young shrubs grow up without fear as fresh and beautiful as anywhere, and all faith in their prosperity not being lost, there fortunately are still found persons who plant them. Absolute destruction is caused only by the direct action of the smoke, but a general weakness may be seen extending far beyond this, resulting in a less capacity of resisting the attacks of external influences.

As to the effect on the inhabitants, the question becomes exceedingly complicated, but the registrar-general's returns are an unanswerable reply as to the result of the total influences of the district. Few people seem clearly to picture to themselves the meaning of a decimal place in the percentage of death, and few clearly see that there are districts of England where the deaths at least in some years, and when no recognised epidemic occurs, are three times greater than in others. When we hear of the annual deaths in some districts being 3·4 per cent., and in the whole of England 2·2, it is simply that 34 die instead of 22, whilst even that is too slightly stated, as the whole of England would show a lower death-rate if the towns were not used to swell it.

One of the conditions of health, and a most important, if not the most important of all, is to be found in the state of the atmosphere.

Combustion of the Carbon.

According to the best founded data, there are burnt in the course of a year in Manchester two million tons of coals. Now, supposing the district in which it is burnt to be 4 miles square or 16 square miles, and the height of atmosphere which is used by the inhabitants to be 60 feet, and the amount of carbon in the coal to be 75 per cent., we have introduced into this region in the course of a day 15,066 tons of carbonic acid or 1·6499 per cent. of the air. Now, it may be said that the region is not correctly laid out; that 16 miles is too extensive, and 60 feet is not sufficiently high. In fine weather I believe that the atmosphere is influenced by the smoke at least to the height of 600 feet. If that extent were taken, we should find the amount of carbonic acid equal to 0·16499 of the air. But as a medium will probably be correct, let us say 300 feet high, and the amount will then be 0·33 per cent. of carbonic acid thrown into the air.

The several cases will stand thus—

On a space of square miles, 60 feet high, there is an amount
of carbonic acid from coals . . . = 1·6499 per cent.

To this add the amount already in the air . . . 06

Now, supposing 400,000 inhabitants give out

266 cubic feet of respired air with 6 per cent.

of carbonic acid, there will be 330 tons or .0362

Total carbonic acid . . . = 1·7461

If this were changed ten times a day, the result would be, at any given period,

CO ₂ from coal	. 0.16499
CO ₂ from breath	. 0.00362
Usual amount of CO ₂ in the air	. 0.06
<hr/>	
Total at a given time	. 0.22861

If the air were changed twenty times a day, the result would be—

CO ₂ from coals	. 0.08248
CO ₂ from expired air of inhabitants	0.0018
CO ₂ of the atmosphere	. 0.06
<hr/>	
	0.14428

But as a medium state is common, let us suppose the height to be 300 feet, changed ten times a day, then the result is—

CO ₂ from coals	. 0.033
CO ₂ of expired air	. 0.00072
CO ₂ of the atmosphere	. 0.06
<hr/>	
	0.0937

The average speed of the air at Liverpool is equal to 12.63 miles per hour by the observations of Mr. Hartnup, F.R.A.S., of the observatory there; let us say twelve miles at Manchester. It would sweep over the four miles three times an hour or thirty-six times in twelve hours.

This would give, with the height of 300 feet—

CO ₂ from coals	. 0.0091
CO ₂ from expired air	. 0.0002
Usual amount	. 0.06
<hr/>	
	0.0692

So that states of the atmosphere occur when the amount is very small when put into figures. Allowing the air outside the town to have 0.03 of carbonic acid, which is rather above the amount found

on the sea-shore and the hills, and allowing the conditions in other respects to be the same as the last-mentioned, we have—

CO ₂ from coals	0·0091
CO ₂ from expired air	·0002
Natural CO ₂	·0300
	<hr/>
	·0393

This is less than the amount which I have at any time found, but may probably be taken as the extreme limit.

When we examine the subject in this manner, we perceive how small is the actual amount of effect which the accumulated efforts of art can produce on nature, and we are inclined to look on the result as not to be regarded. Repeated observations of various chemists have until lately pronounced the air of towns to be equal as far as composition is concerned, to that of the air most distant from human habitations. The experience of mankind has been against this, but it has been believed that science was unable to obtain a method of observation which could equal the test of the human lungs, or still more of the continued action of the lungs during the whole length of even a shortened life. These calculations agree so far with the results obtained that I am disposed to think that each is nearly true in its turn, and that times do occur when the percentage of carbonic acid is as high as in the first supposition. Such periods, however, are of brief duration, or have at least not occurred lately for more than a day at a particular place. When the carbonic acid was estimated by passing the air through a potash bulb apparatus very slowly for a whole day, a similar variety of results was obtained, but in equal weather and equal wind the results were very uniform. During the time the following experiments were being made, the weather was remarkably open and fine, and the results were lower than what I have sometimes calculated for the air outside the town.* When there is much wind blowing, they average from 0·045 to 0·08 per cent.; when less, they average from 0·10 to 0·12; making, the amount of carbonic acid decidedly different from the amount in the country. It still remains a question whether the amount is capable of affecting human life, and if the effect of the town atmosphere on health be not wholly attributable to other causes; I still believe that the carbonic acid is by no means the most important cause.

* I ought to have made simultaneous determinations of the air inside and outside the town. I hope to do so.

The carbonic acid was first determined by absorption with potash. The air was previously passed through sulphuric acid and chloride of calcium by an aspirator. The experiments were made at the Literary and Philosophical Society, George Street, Manchester.

No. 1.

February 25.

	Grs.
Total weight after experiment . . .	1906·50
„ „ before „ . . .	1901·64
	<hr/>
Difference . . .	4·86

14·63 cubic feet of air used. $\text{CO}_2 = 0·04095$ per cent.

No. 2.

March 16, 1853.

	Grs.	After experiment. Grs.
Potash bulbs, first . . .	335·280	324·200
„ „ second . . .	482·030	479·000
Chloride of calcium and tube . . .	865·555	879·100
Sulphuric acid apparatus . . .	805·080	810·650
Total weight after experiment . . .	2492·950	
„ „ before „ . . .	2488·665	
	<hr/>	
Difference . . .	4·285	

9·2 cubic feet of air used. $\text{CO}_2 = 0·0573$ per cent.

No. 3.

March 18.

	Grs.	Grs.
Potash bulbs, first . . .	537·760	489·100
„ „ second . . .	413·220	452·60
Chloride of calcium tube . . .	875·00	895·90
Sulphuric acid apparatus . . .	819·79	830·02
	<hr/>	<hr/>
Total weight after experiment . . .	2647·62	
„ „ before „ . . .	2645·77	
	<hr/>	
Difference . . .	1·85	

5 cubic feet of air used $\text{CO}_2 = 0·0455$ per cent.

No. 4.

March 19.

	Grs.	Grs.
Potash bulbs, first . . .	443.00	440.90
" " second . . .	490.00	489.60
Chloride of calcium tube . . .	873.84	880.04
Sulphuric acid apparatus . . .	829.66	831.73
<hr/>		
Total weight after experiment .	2642.27	
" " before " . . .	2636.50	
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Difference . . .	5.77	

4.6 cubic feet of air used. $\text{CO}_2 = 0.1544$ per cent.

No. 5.

March 20.

	Grs.	Grs.
Potash bulbs, first . . .	440.90	440.75
" " second . . .	489.60	489.77
Chloride of calcium tube . . .	877.63	879.60
Sulphuric acid apparatus . . .	829.66	830.72
<hr/>		
Total weight after experiment .	2640.84	
" " before " . . .	2637.79	
<hr/>		
Difference . . .	3.05	

6.91 cubic feet of air used. $\text{CO}_2 = 0.0544$ per cent.

No. 6.

March 22.

	Grs.	Grs.
Potash bulbs, first . . .	439.70	440.75
" " second . . .	474.90	489.77
Chloride of calcium tube . . .	886.00	873.67
Sulphuric acid apparatus . . .	830.80	832.43
<hr/>		
Total weight after experiment .	2636.62	
" " before " . . .	2631.40	
<hr/>		
Difference . . .	5.22	

5.38 cubic feet of air used. $\text{CO}_2 = 0.1195$ per cent.

No. 7.

March 23, 1858.

	Grs.	After experiment. Grs.
Potash bulbs, first . . .	417·575	413·070
„ „ second . . .	393·560	393·342
Chloride of calcium tube . . .	874·050	876·005
Sulphuric acid apparatus . . .	809·200	814·290
<hr/>		
Total weight after experiment . . .		2496·707
„ „ before „ . . .		2494·385
		<hr/>
Difference . . .		2·322

2·256 cubic feet of air used. $\text{CO}_2 = 0·0973$ per cent.

No. 8.

March 24.

	Grs.	Grs.
Potash bulbs, first . . .	393·342	392·950
„ „ second . . .	413·000	412·450
Chloride of calcium tube . . .	876·005	876·442
Sulphuric acid apparatus . . .	814·150	817·012
<hr/>		
Total weight after experiment . . .		2498·854
„ „ before „ . . .		2496·497
		<hr/>
Difference . . .		2·357

2·98 cubic feet of air used. $\text{CO}_2 = 0·0972$ per cent.

No. 9.

March 26.

	Grs.	Grs.
Potash bulbs, first . . .	442·57	462·57
„ „ second . . .	501·28	472·40
Chloride of calcium tube . . .	875·78	875·37
Sulphuric acid apparatus . . .	487·56	499·00
<hr/>		
Total weight after experiment . . .		2309·34
„ „ before „ . . .		2307·19
		<hr/>
Difference . . .		2·15

4·6 cubic feet of air used. $\text{CO}_2 = 0·0575$ per cent.

No. 10.

March 27.

	Grs.
Total weight after experiment . . .	2311·42
„ „ before . . .	2309·34
Difference . . .	2·08
3·83 cubic feet of air used. $\text{CO}_2 = 0·0668$ per cent.	

By these experiments we have—

No. 1	0·0469 per cent. CO_2
2	0·0573
3	0·0455
4	0·1544
5	0·0544
6	0·1195
7	0·0973
8	0·0972
9	0·0575
10	0·0668

Average of carbonic acid = 0·07908

The amount of carbonic acid obtained on the hills near Preston was 0·022 per cent., and another time at Blackpool 0·03. If this were the mean of the air supplied to Manchester, the increase by smoke and other substances would be 0·049 in the centre of the town. I have not ascertained its average condition when it enters Manchester. 0·049 will represent the causes operating over all the county. High winds and stormy weather diminish the carbonic acid very much.

The next peculiarity in the air to which I will call attention, is the sulphurous and sulphuric acids, and to judge of this, I have here given analyses of various coals used in Manchester.

The Sulphur.

The table gives the analyses of 71 specimens, some of which have amounts of sulphur as high as 5 and even 6 per cent.; but leaving out these, we have from 66 specimens of coals used in Manchester, an average of above 1 per cent. of sulphur; or

let us say, 1 per cent. as the lowest amount we can be allowed to assume. If we take 1 per cent. as the average amount, we have 54.79 tons of sulphur burnt daily, producing 167.8 tons of sulphuric acid. This would give in the assumed space of 16 miles a grain of sulphuric acid to 101.72 cubic feet or 1 in 54,455 grains, or 0.0018367 per cent. by weight: by volume it would appear much less.

Amount of sulphur in coals used in Manchester.

Sulphur per cent. = SO_3HO

1. A mixture of equal parts of 32 specimens of coal gave an average of sulphur =	1.4208 ..	4.3509
2. Average in a mixture of coal used by 17 of the largest consumers	1.1512 ..	3.5255
3. Average of another mixture of 9 coals	2.3188 ..	7.1957
4.	0.502 ..	1.5374
5.	2.399 ..	7.3487
6.	2.224 ..	6.811
7.	4.965 ..	15.2071
8.	2.034 ..	6.2303
9.	2.951 ..	9.038
10.	1.008 ..	3.087
11.	6.197 ..	18.9789
12.	5.308 ..	16.258
13.	2.158 ..	6.610
14.	0.602 ..	1.8462
15.	1.227 ..	3.7583
16.	0.508 ..	1.5557
Average of 71 specimens	1.665 ..	5.099
Average of 64 specimens, the 7 highest being removed	1.43 ..	4.37
1 per cent gives of sulphur =		3.0625

Sulphur-acids in the air.

In order to obtain the amount of sulphurous and sulphuric acids, I passed the air through acetate of lead. The mode of experimenting here also was to draw the air slowly through the solution, taking care to have a sufficient number of bulbs. Two of Liebig's potash apparatus were quite enough, the last bulbs having no deposit. The water drawn off by the aspirator was measured.

128·8 cubic feet of air gave, with acetate of lead, a precipitate of sulphate of lead = 0·2

60 cubic feet gave 0·095

The first is equal to 1 grain of sulphuric acid SO_3HO in 2000 cubic feet.

The second is equal to 1·076 grains in 2000 feet.

This by weight is 0·0000934 per cent., or say 0·0001 per cent.

These experiments were made whilst the air was dry, or at least whilst there was no rain; the passage of the air through the lead solution being always interrupted during wet weather. An experiment lasted generally for about two months.

The above were made at my laboratory at All Saints, in a situation where an average of the four miles of district might be expected.

Others in the centre of the town at the Literary and Philosophical Society gave—

1st. 0·0042 per cent. of SO_3HO

2nd. 0·0017 „ „

The first of these determinations was made whilst the weather was rather moist, and the acid would probably fall, whilst a moist atmosphere, with as much acid as it could obtain, would pass into the solution. The second is very little below the calculated amount. The amounts differ considerably, but the smell has long ago decided on the fact of a great variation in the amount. One is surprised after all at the minuteness of these figures.

At the same time, the amount calculated is, in my belief, much too high, for an average; and there is another method by which we may find an explanation of the fact that a smaller amount is obtained by experiment.

On examining some smoke from chimneys, I found that in 100 cubic feet (reduced to 65°F.), there were—

	Sulphur in grains.		SO_2		SO_3		SO_3HO
1.	8·13	=	16·26	=	20·325	=	24·05
2.	11·925	=	23·850	=	29·812	=	36·522
3.	2·666	=	5·322	=	6·653	=	8·150
4.	2·635	=	5·271	=	6·529	=	8·072
Average	6·328	=	12·651	=	15·829	=	19·1986

These I consider examples of the amount of sulphur from

chimneys giving out a large amount of sulphur, and others giving a comparatively small amount. As the amount of carbonic acid was not under 4 per cent., it is clear that all the sulphur actually in the coal is not made apparent in the smoke by this mode of burning. Mr. Spence, of Manchester, first called attention to the probability that the amount of sulphur-acids would greatly increase if the smoke were thoroughly burnt, believing that the sulphur is driven off at present uncombined in company with the carbon. In the few specimens of soot which I have examined, I have not found free sulphur. Sulphuretted hydrogen is rare, and cannot account for the absence of sulphurous acid, and sulphuret of carbon, which is produced by the distillation of coal, may be the chief mode by which sulphur is removed, as Dr. Bernays suggested to me. Although then it seems to be shown that a great portion, if not all, of the coal used is burnt in such a way as not to give its maximum of sulphur-acids, it is also true that from other circumstances, certain districts receive even more than their average into the atmosphere. I am ready to believe, then, that the evils arising from sulphur-acids in the air are somewhat diminished by the wasteful and offensive method of burning coals now practised; but the diminution is not sufficient to be looked on as a cure, and it may be even questioned whether the black carbon sent into the atmosphere does not produce worse results. I have spoken chiefly of sulphuric acid as the medium of removing the sulphur, and I am disposed to view it as the chief if not the only final product. I have always obtained the sulphur in that state; it seems to be rapidly oxidized when mixed with large volumes of air. At the same time it is well known that sulphurous acid is the form in which, to a large extent, the sulphur is removed by the chimneys, and that for a time it exists as such in the air. It requires no more than the ordinary senses to decide this question. The mode of oxidizing the sulphurous acid may be simply by the immense excess of oxygen supplied, but it may also be oxidized by the ozone of the atmosphere. In doing this, the ozone itself would be destroyed. This could be done by an amount equal to 8 of ozone for 49 of sulphuric acid, or say $\frac{1}{6}$, an amount sufficiently small to be readily supplied.

Ozone.

As to ozone, repeated attempts have failed to discover any indication near my laboratory and in one or two other parts of the

town. At the distance of nearly one mile, I found distinct indications in about two hours, at the sea-side (Blackpool) in less than half an hour, and even on the paper left on my bedroom table at that place during the night. This remarkable substance furnishes a sufficient proof of a distinct difference in the quality of the atmosphere in these places; its absence alone would completely destroy all attempts to prove that the air is not perceptibly altered by towns. At Rochdale, when the east wind was blowing from the hills, there were indications of ozone in a short time, or in less than an hour. At the same place, when the wind was blowing from the town and from the great manufacturing district west of it, no indications were perceived.

Acidity.

In pure air at the sea-side (Blackpool) litmus paper was made slightly less alkaline by exposure for a whole night during a sea-breeze. In other words, the blue colour was somewhat diminished.

In Manchester, blue litmus paper becomes red in half an hour at most, sometimes in ten minutes.

In my earlier papers on the rain, I mentioned that I frequently found alkaline rain. I did not at that time try the experiments so far in the town; my present laboratory is only a few hundred feet nearer the chimneys, but I see the effect distinctly. Polished brass apparatus does not keep so well, and the rain is always acid; of late years I have found no alkaline rain in any portion of what is actually the town. The amount of acidity is such as to colour blue litmus at once; one drop falling on the litmus at once reddens it. One may, by this very simple means, obtain a very clear idea of the extent to which the air is deteriorated by smoke from coals containing much sulphur.

The acidity of the rain in various districts of Manchester was measured for an object to which I was led in the course of my profession. An alkalimeter was used, and a solution of alkali containing one grain of carbonate of soda to 1000 grains of water. 1000 grains by measure of the water to be tested were used; it was boiled in a flask during the process of testing, and mixed with a solution of litmus, previously taking care to ascertain how much acid was required to acidify or redden the amount of litmus used, so as to subtract it from the number obtained. It is generally better that experiments to be compared

should be done by the same person, as the eye gets accustomed to its own peculiar method of judging of shades, and arrives at the results with wonderful constancy.

Pendleton, N.W. district of Manchester.

Wind blowing to the town, 1000 grs.		
of rain water rendered acid by	. 6	of the alkaline sol.
Not directly from the town	. . 16	„
Wind touching the outskirts of the		
town 17	„
From town 36	„
From country 0	„
At All Saints' Church 24	„
„ „ 38	„
For a short time 140	„
Then fell to 40	„
Next to 40	„
And lastly 16	„

Ancoats.

1000 grs. of rain saturated by	. 44	of alkaline sol.
„ „	. 20	„
„ „	. 57	„

Average 40

The rain in these cases was collected in porcelain vessels. In the following it was merely taken out of stone-cisterns, which the inhabitants generally use for collecting water from the roofs of the houses. It will be seen that the results are similar. The weather being wet and the water frequently drawn off, there was little time for evaporation.

Water from cisterns in Pendleton.

No. 1.	1000 grs. of rain					
	water required	6 of alk. sol.	No. 6.	..	64 of alk. sol.	
2.	„ „	5 „	7.	..	46 „	
3.	„ „	6 „	8.	..	40 „	
4.	„ „	10 „	9.	..	12 „	
5.	„ „	38 „	10.	..	14 „	

Average 25

Going over a part less built upon, the variations were according as chimneys were met with on the way or otherwise.

No. 1. 1000 grs. of rain

water required			24 of alk. sol.	No. 5. . .	0 of alk. sol.
2.	„	„	21 „	6. . .	39 „
3.	„	„	0 „	7. . .	0 „
4.	„	„	27 „	8. . .	15 „
				9. . .	28 „

Average 17

Lower Broughton.

No. 1. 1000 grs. of rain

water required			8 of alk. sol.	No. 5. . .	21 of alk. sol.
2.	„	„	33 „	6. . .	23 „
3.	„	„	26 „	7. . .	29 „
4.	„	„	12		

Average 21

Hulme.

No. 1. 1000 grs. of rain

water required			31 of alk. sol.	No. 8. . .	29 of alk. sol.
2.	„	„	26 „	9. . .	36 „
3.	„	„	32 „	10. . .	28 „
4.	„	„	34 „	11. . .	47 „
5.	„	„	49 „	12. . .	34 „
6.	„	„	27 „	13. . .	41 „
7.	„	„	33 „		

Average 34

Salford.

No. 1. 1000 grs. of rain

water required			10 of alk. sol.	No. 8. . .	21 of alk. sol.
2.	„	„	6 „	9. . .	22 „
3.	„	„	50 „	10. . .	28 „
4.	„	„	0 „	11. . .	20 „
5.	„	„	51 „	12. . .	22 „
6.	„	„	6 „	13. . .	23 „
7.	„	„	26 „	14. . .	10 „

Average 21

Ardwick.

No. 1.	1000 grs. of rain				
	water required	24 of alk. sol.	No. 3. . .	24 of alk. sol.	
2.	„ „	40 „	4. . .	45 „	
Average 33					

Ancoats, containing numerous mills and inhabited by a working population only.

No. 1.	1000 grs. of rain				
	water required	41 of alk. sol.	No. 5. . .	24 of alk. sol.	
2.	„ „	28 „	6. . .	28 „	
3.	„ „	60 „	7. . .	68 „	
4.	„ „	40			
Average 41					

The average number is 28·5 for the whole.

Over 16 miles and with a rainfall of three feet deep we have 971, or say 1000 tons of sulphuric acid falling in rain during the year. As we had over this space burnt sulphur equal to 1 per cent. on the coal, it would give an amount equal to 61,245 tons of sulphuric acid in a year. The rain therefore returns only 1·588 per cent. of the quantity produced. But let us suppose that it rains one-sixth of the year, that time will receive all the benefit of the purification, equal to 9 per cent., and certain portions still more, according to the amount of stagnation of the air. As an example, the first rain falling on a particular occasion was at 1·40, but soon fell down to 40 of acidity; and during a violent shower, I found the carbonic acid of the air to be only 0·056 per cent., whilst the rain contained 7·23 cubic inches per gallon.

General Impurities in the Rain.

The rain was found to vary a good deal in the amount of its impurities. The following gives the number of grains per gallon:—

Rain at All Saints	7000 grs.	inorganic	0·265 grs.
Aug. 1857.	2000	organic matter	0·25
		inorganic	0·1
Ancoats	1000 grs.	organic	0·1
		inorganic	0·8

Pendleton	4000 grs.	organic matter	0·19
		inorganic	0·14
			<hr/>
			0·33
Rain at All Saints	10,000 grs.	organic	0·34
		inorganic	0·66
			<hr/>
			1·00

The inorganic matter consisted of:

Peroxide of iron	.	0·245
Sulphate of lime	.	0·177
and rest not ascertained	.	0·238
		<hr/>
		0·660

The inorganic matter is chiefly coal ash. The organic matter is partly products of the distillation of coal.

Mode of Estimating Carbonic Acid.

When examining the action of the manganate and permanganate of potash on sugar, the points that seemed to me most remarkable were, first, that very minute quantities of carbonic acid converted the green into the red acid; and next, that very minute quantities of organic matter entirely destroyed the latter. When a carbonate of an alkali containing more than an equivalent of carbonic acid is added to the manganate of potash or soda, a decomposition ensues, and it is at once rendered red. This salt, called the mineral chameleon, has long been remarkable for this sudden change of colour. When poured into water, apparently and really pure for all ordinary purposes, its appearance is entirely changed, and it is in fact decomposed. But it will be found that water has only a limited power of changing it, and this power depends on the amount of carbonic acid and organic matter. If these be removed or if they be destroyed by the manganate, an additional amount may be employed without any change whatever taking place. Forchammer, in fact, proposed to use permanganate of potash as a mode of estimating organic matter in water, and the method has been less adopted than it deserves to be.

It occurred to me to use this susceptibility to carbonic acid as a mode of estimating its amount. When the manganate of potash is dissolved in water, enough being added to give a bluish purple tinge, the solution may be kept in well stoppered bottles without

apparent change for at least many weeks; but if frequently used it will not keep so long without change. The greatest care must be taken when working with it that no breath should blow upon it, and that no foul air of any kind should approach it. If it is to be transferred to another vessel, that vessel must previously be rinsed out with a portion of the manganate solution, as any water which can ordinarily be used for washing a bottle will destroy some of the solution, and it is better to throw that decomposed part away at once.

A standard solution of carbonic acid was made by filling a bottle with hot and well boiled water, and when cool, adding bicarbonate of potash. The solution first made contained 2·1227 grains of the salt in 5500 grains of rain water. (The bicarbonate of potash gave by analysis 44·98 per cent. of carbonic acid by the common method of loss of weight). This solution will then contain 0·48645 grains of carbonic acid not wanted to form the protocarbonate.

A solution of blue manganate was then made very dilute. Of this 50 grains were reddened by the bicarbonate solution—

1st	.	.	.	850 grains
2nd	.	.	.	846
3rd	.	.	.	848

As each grain of the solution is equal to 0·0000884 of a grain of carbonic acid, I look on these numbers as identical. It would be affectation, but no greater accuracy, to make them arrive within one grain each time.

Having obtained constant results on remarkably minute quantities, the test was then tried with gaseous carbonic acid; the results of these trials I do not find by me at present, but they were equally minute with those obtained by means of bicarbonate of potash, and more so than could be obtained without much trouble by the ordinary methods.

It was believed that the solution coming in contact with the acid of the atmosphere would cause a reddening with so much delicacy that the amount of carbonic acid might be estimated. The experiment was made in a bottle of known capacity, the air being extracted by pumping it out from the bottom and so allowing a fresh current continually to enter. It is safer to fill it by extraction than by forcing, as the pump is apt to communicate some modification to the air.

Another solution of bicarbonate of potash was prepared by dis-

solving 21·227 grains of the pure crystals in 5,500 of prepared water. Each grain would contain 0·001802 cub. in. of available carbonic acid. A solution of manganate of potash was made, 73 grains of which were reddened by 100 grains of the bicarbonate solution. The following experiments were then made to estimate the amount of carbonic acid in the air in the centre of Manchester.

87	cub. in. of air decomposed	35	grs.	$\text{CO}_2 = 0\cdot0981$	p. c.
87	„	36	„	$\text{CO}_2 = 0\cdot1012$	„
87	„	34	„	$\text{CO}_2 = 0\cdot0955$	„
87	„	32	„	$\text{CO}_2 = 0\cdot0899$	„
87	„	33	„	$\text{CO}_2 = 0\cdot0927$	„

In a closed up and crowded railway carriage 0·3484

These are my earliest results and seem rather high. I have nevertheless retained them; since that time there being a good deal of high wind or wet weather, no such amount has been obtained, and a few days ago I obtained the following very moderate results.

May 17th, a very wet day, gave with another solution, the following results:—The solution used had the following strength:

50 gr. of manganate solution -- 140 of the $\text{KO} \cdot 2\text{CO}_2 = 0\cdot01232$ of CO_2 or each grain of manganate equal to 0·000601 per cent. of carbonic acid when 87 cubic inches were operated on.

1.	87	grs. of manganate	=	0·0522	of CO_2 in the air.
2.	91	„	„	0·0546	
3.	95	„	„	0·0570	
4.	94	„	„	0·0564	
5.	98	„	„	0·0588	
6.	97	„	„	0·0583	

Next day was very dry, the air clear, and the wind high, the amount is still small. The experiments were not made together.

7.	113	grs. of manganate	=	0·0679	CO_2 in the air
8.	156	„	„	0·0937	
9.	118	„	„	0·0709	
10.	118	„	„	0·0709	

On a very wet day in a part of Manchester where a great deal of carbonic acid might otherwise be expected, viz., Oldham-road:—

11.	116	grs. of manganate	=	0·0717	CO_2 in the air
12.	120	„	„	0·0721	
13.	110	„	„	0·0671	

An error of 1 grain by measurement makes a change only in the 3rd or 4th decimal place, so that it becomes inappreciable.

Experiment 1—6 inclusive were at my laboratory, the wind blowing towards the town; from 7 to 13 at the other side of the town; the wind blowing violently, and allowing no accumulation, we may conclude that the air of Manchester is very slightly affected by carbonic acid, and certainly this condition, which is equal to a diminution of between 0.04 to 0.08 per cent. of carbonic acid is very decidedly perceptible on the health and spirits: violent rain tends still further to remove the acid.

This mode of looking for carbonic acid of course makes no allowance for the other acids, but gives the total acidity. The other acids may be ascertained separately and subtracted. The amount is too minute to affect the value of these experiments. The method will be valuable in deciding exactly as to the quality of offensive matter issuing from manufactures, where it has hitherto been difficult to obtain sound chemical evidence, although the existence of even strong acid vapours could readily be detected by the senses. To separate the stronger acids from the carbonic I purpose using carbonates for absorption, boiling off the carbonic acid. The two experiments will give the amount of each. This, however, I have not yet put into practice.

The reaction with manganate of potash requires great attention to peculiar shades of colour, and in the hands of persons the most careful, not much accustomed to it, it may not lead to exact results. I have been desirous therefore of finding a substance very highly coloured, and yet capable of being decomposed entirely by carbonic acid. This I have found in the rosolates of the alkalies. Rosolic acid in combination with alkalies gives an amazing depth of colour. I published lately a short memoir* explaining its formation, and showing how it might be made in abundance. In attempting to fix the colour on cloth, it was found that however bright and beautiful it was at first, a short time completely converted it into the mere colour of the dark resin uncombined with alkali. This decomposition is effected by the carbonic acid of the air, and I am inclined to think that the method by the rosolates will meet with more general acceptance than that by the manganate, not because of greater exactness, but because of the more definite limit of the colour. As far as my present observations have gone, there is one drawback to the rosolates, and that is, the greater time

* Memoirs of the Literary and Philosophical Society of Manchester, vol. xv. p. 1.

needed to effect the thorough change; but this requires a little more experience.

Estimation of Organic Matter.

I have been trying for some time to obtain a measure of the amount of organic matter in the atmosphere. Among the first experiments with the manganates were the following, where an undetermined solution of permanganate of potash and manganate was put into a bulb-apparatus, the air being drawn through it by means of an aspirator. It was soon found that results under similar conditions could be relied upon as constant.

Although these first numbers may be of some use as comparative results, I am not inclined to rely on them as giving absolute differences, until it is known what effect pure air would have, acting in exactly similar relations. That the results are correct in a comparative point of view, is shown by the fact of the manganate of the first series of bulbs being more decomposed than that of the second series. I believe the time allowed by this method is not sufficient to enable the decomposition to take place so that a diminished result is obtained, and again I am not sure as to the actual effect as before stated of pure air. The results nevertheless have their value as an approach to the next part of the subject. The air was drawn by an aspirator through a solution of putrid flesh.

Air from putrefying matter.

1.	0.38	cub. ft.	decomposed	250	grs. of a solu-
					tion of permanganate of potash
2.	0.84		"	250	"
3.	0.96		"	250	" drawn through slowly
4.	0.96		"	250	"
5.	0.96		"	250	" drawn very slowly
6.	0.88		"	250	" very rapidly
7.	0.57		"	175	"
	0.81		"	250	"
8.	0.48		"	175	"
	0.68		"	250	"

In this case I did not attempt to approach more gradually than by steps of 25 grs., so that amounts nearly the same become as if identical.

Air from near an Ash-pit and Midden:—

1.	1.15	cub. ft. decomposed	250	gr. of the solution of permanganate of potash.
2.	1.15	„	250	„
3.	0.76	„	175	„
	1.08	„	250	„

Air from the lungs was found to decompose the manganate with much greater rapidity than common air.

It occurred to me then to use it as a test, not upon paper like litmus, as it will not exist in contact with organic substances, but on pieces of porcelain, so that we might judge of the impurity of the air by the time required for decomposition; but the surface rapidly dried, at least when a soda salt was used, and the crust protected the under portion from any change. Afterwards nitrate of ammonia was added to keep it moist, but it was very difficult to obtain a surface on which the liquid would lie uniformly. It would be necessary to have it in constant revolution to keep up a uniform depth. By fixing a porcelain slab, moistened with permanganate to the centre of the hands of a clock, the effect might be obtained if wanted.

But in reality this is scarcely desired, as the method afterwards adopted is not a great exercise to the patience, neither could we make any exact approach towards estimating the amount of air that came in contact with the slab or surface as it would change with the state of the wind or other currents.

I came at last to the use of a single bottle or vessel of air, to be filled by means of an exhauster, as explained when speaking of the estimation of carbonic acid. In the stopper are two holes, each with tubes passing through them. As a stopper I have provisionally used only a cork, a very objectionable substance, but it is possible to avoid all contact between it and the manganate solution. One tube is fitted with a stopcock below, close to the stopper, the liquid is poured into the upper part and allowed to drop into the bottle by opening the stopcock as it is wanted. The lower part of the tube projects an inch or two into the bottle, and is drawn out to a fine point so as to keep it filled until pressed down by the column above, on the opening of the stopcock. The other tube has connected with it an india rubber tube and clasp. Its object is merely to allow a little air to pass out when the liquid is passing in. But the amount of liquid required is so small that this opening is scarcely necessary, the pres-

sure of the few inches of column being generally enough to secure an entrance. The stopcock and the mode of joining the tubes are matters of importance. The ordinary metals cannot be used as they so rapidly deoxidize the manganates, and glass is troublesome and apt to break. I have, therefore, obtained stopcocks of a substance not hitherto used by chemists generally, viz., hard vulcanised caoutchouc made by Mackintosh. I expect great advantages from its use in chemical apparatus. It resists the action of nearly all the agents against which we have to defend our vessels at the ordinary temperatures, and is hard enough to be used for any ordinary purpose. I put one of these stopcocks into a manganate solution, and could see no result till a much greater time had expired than the experiment will ever require. Nearly the same may be said of common india rubber, although it cannot be used for stopcocks; common vulcanised caoutchouc cannot be used for a moment for this purpose in contact with the manganates. It is sometimes convenient to close the upper part of the tube into which the liquid is poured. This is done at present by a gutta percha stopper, but a caoutchouc stopper or stopcock would be equally convenient, if not more so.

Having a little burette which held 140 grs., I poured the whole into the bottle and shook it, not knowing, of course, how much might be required. When the whole effect was supposed to be produced, the bottle was opened, and the air sucked out, not having at the time a suitable pump.

By this means it required the bottle to be filled 16 times before the whole of the solution was decomposed. The experiment when repeated still gave 16 times. It seemed therefore a result which could be relied upon as constant.

In extracting the air from the bottle so as to allow the entrance of the external air, a great excess is of course used, and the surface of the liquid is exposed to a little more decomposition than is just to the experiment, but the results are, independently of this, so fine that I have not practically seen the evil, although it was afterwards guarded against. Besides, as the same amount is used in every experiment, the comparative results are not injured even if it is not guarded against. After using a flexible pump or inverse bellows to extract the air, 140 grs. of the solution were always decomposed by 9 bottles of the air at my laboratory. This method was used in all cases afterwards. The air is pumped out and the external air fills the bottle. The use of the mouth for the purpose

is only mentioned to guard against an imperfect mode of doing the experiment, as well as a process very fatiguing to the lungs.

When air is exceedingly pure, as upon the hills or on the sea-shore, it may be impossible to perform the operation in one bottle, even by the use of the smallest convenient amounts of solution. But as the process will probably be wanted most where the air is impure, the same mode may be used as is described for trying the carbonic acid, and the whole experiment finished by one act instead of repeated fillings.

The first experiments give chiefly multiples of a full vessel of air, as I had no hope of arriving at anything finer. The actual limit of delicacy I am not yet able to give. To obtain a standard solution of permanganate for the purpose of testing organic matter, ten grains of sugar were boiled with acid to render it uncrystallizable; when neutralized it was dissolved in 10,000 grs. of water; 54 grs. of this solution, or 0.054 of sugar calculated as cane-sugar, decomposed 700 grs. of a dilute solution of permanganate of potash. Every ten grains of the permanganate are therefore capable of decomposing 0.000771 of sugar.*

This solution being used, the following results were obtained:—

1. Air from my laboratory, All Saints. 140 grs. of solution decomposed by 783 cubic inches of air, or 9 bottles.
2. Air from the front of the laboratory or open street. 140 grs. decomposed by 800 cubic inches, or $9\frac{1}{4}$ bottles.
3. Air from the back yard. 140 gr. decomposed by 658 cubic inches, or $7\frac{1}{4}$ bottles.
4. Air, from a bedroom (11 ft. \times 10 \times 12) up two stairs and looking to the back; at night. 140 grs. decomposed by 701 cubic inches, or 8 bottles.
5. In the morning, air from same room, in which a young man, aged 20, had slept, 614 cubic inches, or 7 bottles.
6. Front room of laboratory again. 833 cubic inches, or $9\frac{1}{2}$ bottles.
7. Back of Medlock river, behind some small and not clean houses. 140 grs. decomposed by 479 cubic inches, or $5\frac{1}{4}$ bottles.
8. St. Michael's-place, back Irk-street, a closely built neighbourhood, air from back yard. 140 gr. decomposed by 87.7 cubic inches, or 1 bottle.

* I now use oxalic acid, but the whole process must be separately described, and the standard employed fully explained.

9. Inside a rather cleanly kept house, in St. Michael-place, but close to the back yard. 175 cubic inches, or 2 bottles.
10. Front of the house. 438 cubic inches, or 5 bottles (nearly).
11. Air on the high grounds at Hoghton-tower, near Preston. 140 gr. decomposed by 1929·4 cubic inches, or 22 bottles.
12. 50 grs. decomposed by 701 = 140, for 22·4 bottles, or 1962.
13. Same air 50 gr. decomposed by 793 = 140 by 2084 cubic inches.
14. Same air 50 gr. decomposed by 701 cubic inches = 140 by 1962 cubic inches.
15. In a close carriage full of passengers, windows and doors closed, 140 gr. decomposed by 175 cubic inches, or 2 bottles.

Supposing the sugar and the organic matter in the air were decomposed by exactly the same amount of manganate, a supposition which cannot be perfectly true, but which from the minuteness of the amounts, leaves no room for a great error, the quantities of organic matter in the air would be in those cases such that the 140 grs. given would be decomposed by 0·0108 grs. of organic matter. When this is decomposed by 1 bottle or 87 cubic inches of air, it is equal to 1 gr. in 8058 cubic inches of air, or let us say 8000. The amount of organic matter in the atmosphere will then exist in the following amounts:—

	cub. in.
1. Air at All Saints inside the laboratory 1 grain in	72,000
2. Front of the house „	74,000
3. Behind the laboratory „	60,000
4. Bedroom looking to the back „	64,000
5. Same room in the morning after being slept in „	56,000
6. Front of laboratory again „	76,000
7. Back of the Medlock behind dirty houses „	44,000
8. St. Michael's-place behind a house „	8,000
9. Inside a house at St. Michael's-place „	16,000
10. The front of the house „	40,000
11. High grounds 30 miles north of Manchester „	176,000
12. „ „ „ „ „ „	183,000
13. „ „ „ „ „ „	209,000
14. „ „ „ „ „ „	183,000
15. Closely packed railway carriage „	8,000
16. When the strong smell of a sewer entered my laboratory „	8,000

Leaving out the three cyphers, we have a range of from 8 to 200, and I feel assured that we may go much lower than 8 as I entered no spots which were very revolting.

The amount from putrid matter, when coming after these, will shew the great evils to which we may be exposed, and the effects of different positions with regard to it.

The table of putrid matter on page 217, when put in this form gives,—

1.	One grain of organic matter in	20·5	cubic feet.
2.	„ „	45·0	„
3.	„ „	51·9	„
4.	„ „	51·9	„
5.	„ „	51·9	„
6.	„ „	47·5	„
7.	„ „	43·7	„
8.	„ „	36·6	„

It will be observed how much greater it is at first, but how the passage of air over it diminishes it. I may mention that this putrid matter was liquid, and the air bubbled through it, stirring it up. This removed the volatile matter and less than half the amount was after a time found in it. But on being allowed a little rest, the putrefaction began again and increased. The putrefying matter was not in an extreme condition, it was to a great extent expended when I began the experiments.

The air of ash-pits, or rather of middens and cesspools such as the repositories of fæces essentially are in Manchester, was tried, and gave

	grs.	cub. ft.
1.	1 of organic matter by the above mode of calculation in	62·2
2.	1 „ „ „	62·2
3.	1 „ „ „	58·9

The regularity here is remarkable; we may arrive at the exact amount sent into the air per day by these places, but this I have not yet done. Although, as I said before, I do not rely much on the experiments made on the putrid meat as far as amount is concerned, the results look probable and give a range between the purest air and that from putrid matter of from 20 to 180,000, or from 1 to 9000 units.

It would result from this that by breathing impure or putrid air, we might be inhaling 9,000 times more of some organic substance or other than we should be doing by inhaling the purest air.

But without taking such high numbers, and leaving out those experiments on which I have not professed a reliance, and leaving entirely such putrid matter as I have referred to, we have in different air breathed by people in the same county, a substance the amount of which in one case is 22 times greater than in the other, and in air breathed by people in the same town a difference which is as 9 to 22.

These differences are not greater than are required in order to enable us to account for the numbers which represent the deaths of the various districts. In the district in which the highest numbers here given were obtained, there were, in 1855, 4·5 deaths in a hundred, whilst the average is 2·2 for the country. In other words, the number 22 which I have obtained is not more than is needful to account for a state of things which destroys nearly 60 per cent. of the population. At the place where the number $9\frac{1}{2}$ is given, the deaths are not so high as the average of Manchester.

I find the action of the manganates to be much more rapid on sugar when it has lost its *catamorphous** condition by being boiled with acid. The action is then instantancous or nearly so. With crystallizable sugar it is slow. I have not yet decided how far this property may be relied on as a means of testing the amount of crystallizable sugar in a syrup. The action generally is more rapid on bodies tending to decay, and to some extent is a measure of the condition of bodies. This peculiar property may possibly be so far made use of as to enable us to arrive at some idea of the condition of a miasm or epidemic virus. If exceedingly active, it may act more rapidly than usual on organic matter. There is, therefore, a field of inquiry here.†

To prevent any doubt as to the fact of the vapours from putrid matter affecting this test, some mutton was put into a large closed vessel and allowed to putrify. Some of this vapour, even after many days, as well as some after many months, being collected in a tube and treated with manganate of soda, instantly decomposed a very large amount, leaving, as it appeared to me, some organic matter which was not entirely resolved into an oxide of carbon and water; but as these experiments are intended for another inquiry, it is enough for the present purpose to show that decom-

* I have used *catamorphous* in opposition to *amorphous*. Hitherto there has been no equivalent: crystalline and others are only so in a restricted sense. *Catamorphous* or *Katamorphous* includes crystallised and crystallisable substances and such as assume a recognisable form, whether well or ill defined.

† I have already found considerable diversity in this respect.

position does take place when the only substance present is in the form of gaseous matter.*

I should not omit to say that we must not lay too much blame on the sulphurous acid of the coals. There can be little doubt that it acts as a disinfectant of the putrid matter in towns, and any one with an attentive smell passing through the streets of this country and the cleanest towns of the continent must feel how vastly superior our atmosphere here is in respect of putrid matter capable of affecting that sense: whilst then there is a great charge against the sulphur, we must not omit to speak so far in its favour. This was first mentioned to me by Mr. John Graham. It seems to me that the statistics of epidemics in large manufacturing towns fully bear out this belief, although a few cases present difficulties which my knowledge of the particulars does not allow me to clear up. It may, however, be said that if the ozone of the air oxidizes the sulphurous acid, it is rendered incapable of oxidizing the organic matter, and so the effect of the one is entirely lost, although the effect of the other is gained. Supposing they equally balanced each other, there still remains the sulphuric acid, to which we must attribute a disinfecting power of great value, although inferior to that of the sulphurous.

The sulphurous acid will readily act on sulphuretted hydrogen, and that gas is, I believe, largely removed from our atmosphere by the acid, and excepting near its sources, is not much to be complained of, never attacking the senses in the streets except in these circumstances. One of its most fertile sources in all towns is the gas-works.

Action of the air on the blood.

No conclusion seems to have been arrived at respecting the exact nature of the effect on the lungs of the atmosphere of large towns and that supplied pure by nature. Many persons believe that no difference really exists, and that the different effects which are supposed to be experienced, arise in reality from the different conditions and occupations of life. Not later than this week, evidence has been given in a committee of the House of Commons, ignoring any such differences. The phenomena which I have just explained will, I trust, put all question aside, although I feel assured that to those who have already studied the subject no proof of actual difference was needed.

* Sometimes the term *manganate* is used when permanganate might be written, but it is not important, although the latter is preferred for organic substances.

The question might now be asked what is the method by which the air of towns affects human life? The answer always has been that it is principally through the medium of the lungs, and that the blood must in time become somewhat altered. That delicate and mysterious liquid has not, as far as I know, been made to explain the reaction.

Finding that an artificial test was capable of indicating the state of the air, it seemed to me probable that the blood being in reality more delicate, at least with the assistance of time, might also undergo some peculiar change which might be made sensible to the eye.

I passed some ozonized air through blood, and found instantly a remarkable reddening. I then passed the common air of Manchester through another portion of blood, and obtained, after a few minutes, a very red colour. The effect of a very small amount of ozone, even a bubble of the ozonized air, was sufficient to give a maximum of brightness. The phosphorus vapours were not removed from the air, and I am aware that many substances in small quantities brighten blood. Of these, phosphoric acid is, I believe, one, but no such marked result was got by the acid alone.

Having familiarized myself with the appearance produced by shaking a measured portion of blood with a given amount of air, with repeated variations for several days, using both new and old blood, I proceeded to try the same at the sea-side. It was found that blood, diluted with an equal volume of water, was most convenient for many of the experiments, for although the colour, and all the changes are somewhat different, the comparative results are exactly the same; it also very much assists the observation to have the results confirmed by both conditions. The blood also keeps longer when diluted. Of course, for many observations to dilute the blood is to destroy it. I had found that the experiments were not altered in character, by using blood two or three days old, or even much older, but I so contrived as to begin the experiments at the sea within three hours after leaving them in Manchester, so that both the eye and the material might come fresh to their work.

I expected that the large amount of ozone in the sea-air would rapidly redden the blood, and that the reddening would be much greater than in Manchester. The effect was otherwise; it was decidedly less, and much less. The trials were repeated at various

periods of the first and the next day, and with uniform results. It was not easily explained, but it was at least satisfactory to know that there was a difference.

Finding that phosphoric acid in small quantities gave a lighter colour to the blood, I tried also minute quantities of sulphurous acid. The blood by this means is made less clear, as it seems to me, of a lighter, but not such a rich red ; after a while it becomes darker.

In order to obtain air perfectly free from the acid impurities of the town, it was passed through caustic soda into a bottle of the same size always used in the experiments, and air from the town was introduced into another. An equal amount of blood was poured into each without removing the stopper, by the means already described. When shaken, it was plainly seen again that the Manchester air caused a greater transparency or a lighter red.

By these experiments, in which I got no contradictory results, I conceive it is shown that the atmosphere of a town has a peculiar effect on the state of the blood, an indication of which is capable of being rendered distinctly perceptible to the ordinary eye. This will, in course of time, act for good or evil on the constitution. I say for good or evil, because, although I do not for a moment doubt the superiority of that condition of the atmosphere which nature has given us to breathe, over all other conditions induced by us, I can imagine that circumstances might arise where such a change as this alluded to might be favourable, or in other words where the atmosphere of such a town would have a favourable curative effect.

Many questions arise on this, and as I am not willing to speculate at present, even if I were sufficiently acquainted with physiology, but rather to inquire further, I shall venture only on a few remarks. In looking over the action of reagents on the blood, a great majority are said to make it red or vermilion. I was almost tempted to inquire whether observers had not mistaken the simple action of the air for that of the reagent, but I found that many acids and alkalies give this light colour under conditions when the action of the air alone could not explain it. May it not be that the abstraction of carbonic acid reddens blood, and that this is performed by the oxygen of the air taking its place in normal conditions, by alkalies absorbing it in certain experiments and by acids assisting its departure in other experiments, and in

the acid air of towns such as described? If so, we have an abnormal reddening caused by acid vapour, but, although greater, not productive of an identical effect, because not effected by the oxygen only which is the agent for the natural decomposition required.

Another supposition I am better pleased with. If acids assist oxidation of the blood in the same manner as they do the oxidation of many other bodies, then they cause the action of the lungs to go on more rapidly and hasten the current of animal life, producing that greater restlessness of the system which is the peculiarity of great towns. I am inclined to believe that by following up this inquiry, such questions will receive a distinct answer. As the blood is such a delicate test, it is highly probable that the true action of various climates will best be known by studying in this manner the direct action of the atmosphere: it is true that an inorganic test capable of similar changes would be more convenient, but many will be needed to supply the manifold character of blood itself, and all the substances that can be used may still produce united effects explaining less than one experiment with blood.

If the true explanation be found in the increased oxidizing effect of the air of towns, the carbonic acid will not be so hurtful in the air as the sulphuric, although the latter exists in such small quantities. Mineral acid fumes, I know, by too much experience, are exceedingly irritating to the nervous system. At the same time, I am not aware of any experiments with carbonic acid and the blood, beginning with a natural, wholesome amount, and rising up by 0.01 per cent. at a time. I tried only a few hastily, with minute amounts, but got no such results as by sulphurous acid.

If then the eye can see those changes in the blood, it is not to be wondered at that those minute portions amongst which chemical changes act, should, by their accumulated agency, influence the whole phenomena of life.

The plan of estimating the carbonic acid will give also every other acid equally, but when it is desired to know of any effect arising from acids stronger than carbonic acid, the blood itself may be used as a test. This, however, in the hands of any one who does not accustom himself to it, may give fallacious results, as the effect is best seen after many comparative observations.

The test for the organic matter will include also sulphuretted hydrogen and some other gases, but I do not suppose that carbonic oxide will be affected by either of the methods. The great sources of evil seem, however, to lie in decomposing animal matter and the acids.

The value of these tests will be known only when it has become a common experiment and an easy one to ascertain the purity of an atmosphere and the efficiency of systems of ventilation, disinfection, and general purification.

I can readily imagine cases in which a fallacious result will be given, when, for example, the air is richly laden with the perfume of flowers; probably the materials producing the odour will be decomposed like putrid matter; but this must be left to further inquiry. Even in such cases, a great preponderance of odour is found prejudicial to the health, and the luxurious perfumes of autumn border closely on and readily pass into unwholesome emanations.

The breath is very variously affected, as we may suppose, by the state of health. I did not, however, find that it was capable in the few cases tried, of decomposing as much manganate as the worst cases mentioned of air out of doors in unclean or crowded places. I found, however, remarkable differences in the amount of organic matter in the breath when sweet and when disagreeable. It is quite possible that this test may be used as an indication of the state of the stomach. In a few cases, I found that its condition was correctly registered.

Oxygen.

As to the amount of oxygen in the air, I fear I have not made a sufficient number of experiments, finding it inconvenient to experiment on air from the centre of the town. I did not adopt the precaution of collecting a certain quantity from one district, and making several analyses of the same specimen; each analysis, therefore, refers to a different specimen in reality, and it was found by the other methods of analysis, that the air is constantly changing in composition, and that these changes were found in the second decimal place at least, and even in the first. Having broken my barometer at the time, I was reduced to use an old one, consecrated certainly by the hands of its former owner, Dr. Dalton, whose old laboratory I used for the time, but not thereby improved in its results.

Cub. C. Air used.	C.C. of H. added.	C. C. After explosion.	Per cent. of oxygen.	
1. 40·731	73·176	— 24·113	=	20·868
2. 45·786	83·482	— 27·405	=	20·179
3. 33·125	74·582	— 20·677	=	20·807
4. 51·618	88·275	— 56·355	=	20·613
5. 93·107	170·240	— 112·150	=	20·793

These are of course the reduced numbers obtained. Leaving out the second, which is probably too small, the average will be 20·770 of oxygen. This will certainly agree with the numbers for carbonic acid very well, but I have, as I said, no evidence of the air being of a similar composition in any one case. I can scarcely call it an oversight, because, until I had become long familiar with the results, I had not become accustomed to view the atmosphere as so liable to frequent changes. The air outside the town should also be examined in connection with this, and until then no conclusion can be drawn as to the exact effect of the chimneys. Dalton's observations (quoted in Gmelin)* were, for Manchester 20·99, 20·95, 20·83; three miles from Manchester, 20·85. My experiments show a little deterioration. This, however, we may fairly say that it is not from any want of oxygen that the air of Manchester or similar towns can be less fitted for health. The amount varies much more with the changes of temperature and pressure, and it is not to be conceived that such a slight change in the proportions could have any effect on the blood or the health. Besides, I consider that the experiment here recorded, where the air was passed through caustic potash, and was found to have lost its peculiar effect on the blood, sufficiently shows that the peculiarity was not caused either by the amount or proportion of the oxygen, as both of them remained unchanged. The diminution of oxygen may be looked on as amounting to from 0·1 to 0·2 per cent. With gusts of smoke this must be higher.

Ammonia in the Air.

I find only one experiment in which the ammonia was directly taken from air. 21·341 cubic feet of air were passed through an acid solution, and on being treated with a platinum-salt, 0·0517 of ammonia were obtained. This is equal to 1 grain of ammonia in 412·42 cubic feet, or by weight 0·000453 per cent., or if saturated with sulphuric acid, 0·001758 of sulphate of ammonia. I have

* Handbook of Chemistry (translation), vol. ii., pp. 407, 408.

made no verification of this experiment; the place where it was made was in an open space at my laboratory, which with a south-west wind receives no smoke from factories. The ammonia here is sufficient to neutralise more than the amount of sulphuric acid found when the wind blows from the chimney districts. It shews, however, that, as in my earlier experiments, an alkaline atmosphere may occasionally be found. It happened, however, in this case that the air was acid, and that much more sulphuric acid was found than was needful to neutralize the ammonia. The sulphuric acid from the same air was intercepted by lead salt. The amount of sulphate of lead obtained was 0·6 grains = 0·2041 of sulphuric acid, and equal to 1 grain in 104·6 cubic feet. This is nearly as much as the theoretical amount calculated for the assumed space of 16 miles, but it must be only occasional. The weather was moist, and in such a state of the air, the acid falls rapidly with the rain, the earlier rain clearing all that is in the air. I do not doubt that in the direct course of the smoke from a chimney, a much higher amount might be obtained, as it becomes then offensive to the smell, and sulphurous acid is strongly perceived. The utmost attainable limit in any given spot must be many times greater even than this.

Rain gave by the instrument, a short account of which I read to the Manchester Philosophical Society:—

Carbonic acid, 5·133 cubic inches per gallon.

„ 7·233 „

„ 7·233 „

„ 7·46 „

By the use of the manganate, I obtained in one case 7·2, and in another the same amount as by the apparatus where the gases are removed by boiling, but the use of the former for water requires many precautions. To obtain correct results the organic matter must first be removed. If this method should turn out as successful as it has promised, the carbonic acid may be taken in 1000 grains of water in a few minutes.

Carbon in the Air.

By examination of several chimneys, I came to the conclusion that about 1 per cent. weight of the coal used is sent off in the condition of carbon or tarry matter. This will be equal to

nearly 60 tons a day. Supposing it to be 60 tons, and the space alluded to filled equally with the vapour, with a thorough change twenty times a day, then only 3 tons would exist in suspension at a time in the atmosphere. This would be only 1 grain in 5,689 cubic feet, or 1 grain in a cube of rather less than 18 feet (17·853). This is sometimes more, sometimes less than the truth, in all probability. It is about the truth for a very clear day. The half of this will be more frequently true. With 1 in 5689, or in the best seasons, we should breathe a grain of soot in twenty-one days: a small quantity, but it is given in irregular doses, and as it has a very large surface, a grain appears very large. The carbon separates from the rest of the smoke much sooner than the gases, and is often seen floating at a long distance from its source, when all the gaseous matter must have been removed, like the skeleton of the smoke alone, without the vitality of diffusion to decide upon any course.

Tarry Matters in the Air.

Besides the carbonic acid, as a result of the combustion of coal, the products of distillation must also be considered. In one case, I found exactly one-half of the carbonaceous matter of the smoke to be volatile. 100 cubic feet gave 8 grains of soot, 4 grains being volatile. If so, the amount which I have given for the carbon and tar, &c., may be stated thus:—

$\frac{1}{2}$ per cent.	of the weight of coal used	given off as carbon.
$\frac{1}{2}$	given off as tar, and
	other volatile products of coal,	all of which may be
		included.
	Or 30 tons of tar per day and 30 of soot,	
	Or 0·83 to 1 $\frac{1}{2}$..	0·83 to 1 $\frac{1}{2}$.. in the atmo-
		sphere at a time.

Now, I have ascertained by experiment that some of these products are capable of decomposing manganates, and when judging of the unwholesomeness of a district by the amount of organic matter, care must be taken not to be misled by this. The error cannot be high, because if there be one-half of tarry matter capable of decomposing a manganate to 100 of coals, then the 99 of coals taken as carbon, which is near enough for the case, will give 363 of carbonic acid, or there will be only 1 of tarry matter to 726

of carbonic acid. The acid must therefore increase enormously before its accompaniment the tar can produce any effect. Besides, only a portion of this tarry or distilled matter is decomposable during the time of an ordinary experiment. It must not, however, be forgotten.

Smoke from common Fires.

1·604 cubic feet of smoke or gases from the chimney of a common fire, when the fire was smoking, gave—

Ammonia	0·0345
Sulphurous acid	0·1229

From a clear fire :

Ammonia	0·0326
Sulphurous acid	0·7047

In the first there is a grain of ammonia in 46·5 cubic feet ; in the second, a grain in 49 cubic feet. It is shewn that the sulphur is burnt in greater part after the smoke has ceased, as common experience indicates. The ammonia does not diminish so rapidly as we might expect. It is, in fact, very difficult to remove the nitrogen from coal or coke. Some experiments which I made on the subject gave a great diversity in the amount, but a low heat seemed to send off very little, and a high heat evidently destroyed entirely a large proportion.

Effect of the Atmosphere on Stones, Bricks, Mortar, &c.

It has often been observed that the stones and bricks of buildings, especially under projecting parts, crumble more readily in large towns where much coal is burnt than elsewhere. Although this is not sufficient to prove an evil of the highest magnitude, it is still worthy of observation, first as a fact, and next as affecting the value of property. I was led to attribute this effect to the slow but constant action of the acid rain. If it affects substances with so great an excess of silica, it is not to be expected that calcareous substances will resist it long, and one of the greatest evils in old buildings in Manchester is the deterioration of the mortar. It generally swells out, becomes very porous, and falls to pieces on the slightest touch. Some mortar in this condition

from a building behind the house of the Literary and Philosophical Society of Manchester was examined.

9.18 grs. gave 7.57 of BaOSO_3 , or 28.33 p. c. of sulphuric acid, = 48.16 per cent. of sulphate of lime.

It is not to be wondered at that iron oxidizes readily, and that galvanized iron is valueless in a district where the acid rain converts it at once into a battery. It will be observed that this style of roofing is preserved in exact proportion to its distance from manufacturing districts.

Iron by itself also becomes readily oxidized in this acid atmosphere. Bronze, too, is rapidly blackened, and articles of brass become affected to a great depth, losing their strength. I suppose the sulphurous acid forms on the surface a coating of sulphide of copper, whilst a sulphate is washed away if exposed to rain.

Carbon on the surface.

The smoke of large towns is guilty of an offence to the eye, and through the eye it offends us both intellectually and æsthetically; in other words, the darkness and gloominess react on the character, especially of those not accustomed to the place, in such a manner as to make them distinctly conscious of a change; those accustomed to it are not conscious of the effect, nevertheless it acts upon them in such a way as to destroy some of the fine instincts of perception of natural beauty. But this is a long subject and a difficult one, leaving room for much difference of opinion. The actual amount of carbon on the surface of Manchester buildings is very small. It collects on the rough surfaces principally, and when mortar is put roughly on, it soon becomes perfectly black, although the red of the brick should remain moderately clear. Rough bricks also take it up in greater quantity, and become black in proportion to their roughness.

4.4 × 4 or 17.6 square inches gave of carbon 0.17 grains.

3. × 2.7 or 8.1 „ „ 0.02 „

The last is equal to 0.45, or about half a pound in a house 30 feet by 30. This is, I believe, a great deal above the mark; at least I believe a house will appear dingy with a minute

portion of this. The experiment should be performed on a larger scale.

The fact that the rough portions retain the carbon suggests a cure, viz.—smooth bricks. Polished or glazed bricks and similar mortar would render the rain capable of washing the carbon off, but certainly it will be much better not to allow it ever to arrive there. The importance of preserving the beauty of the original materials is daily increasing.

Can a Cure be found?

A cure for some of these evils ought certainly to be found. Already one cure for the evils connected with organic matter has been made known to us, and that is the removal of the impure matter by means of water. If disinfection were added to this, it might be made complete. The cure of the black carbon or smoke burning is in the hands of every man. The smoke is always blacker as coal is cheaper. Our towns are not in earnest on the subject.

For the amount of sulphur in the air there has never been any attempt at a cure by any one, nor has it been generally looked on as an evil. A small beginning of this important subject occurred to me whilst investigating a patent obtained by Mr. Holme, of Manchester, for bleaching smoke. In this patent, Mr. Holme claims the use of lime and of common salt mixed with the coals, but finding lime of no value in giving the peculiar white colour to the smoke, he gave it up, and used salt only. On examining the effect of the salt upon the vapour, I found that it diminished the quantity of the sulphurous acid given off, and on examining the effect on the ashes, I found a greater amount of sulphur in them than when otherwise treated. I give here the result of a few experiments made to ascertain the action of salt and bases.

Amount of sulphur driven off from a specimen of coal by distillation:—

Coal alone.

- | | |
|--------------------------|------------------------------|
| 1. At a low red heat, | 0·4692 per cent. of sulphur. |
| 2. At a higher heat, | 0·5655 „ |
| 3. At nearly white heat, | 0·6755 „ |

Coal with common Salt.

4.	With 5 per cent. salt,	0·4526 per cent. of sulphur.
5.	Ditto, at higher heat,	0·4843 „
6.	Ditto, nearly white,	0·5557 „

This makes a difference of 18 per cent. in the amount of sulphur sent off, the least being sent off by the mixture of common salt. It has, in fact, been long known that sulphur decomposes common salt, at least when the elements of water can be readily supplied, but still more may we expect it when carbon, &c., assist.

The remainder, or cinder, contained :—

From No. 3	..	0·4332 per cent. of sulphur.
From No. 6	..	0·5448 „

Finding this result, it occurred to me that lime would be a much more efficient substance for retaining sulphur, the salt, on account of the white fumes given out, being entirely inadmissible. I distilled some coal with the following result:—

Coal distilled alone	.	0·4338 per cent. in the distillate.
Coal with 5 per cent. lime	0·1754	„
Coal with 10 per cent. lime	0·0511	„
Coal with ditto	.. 0·0616	„

It results from this, that Mr. Holme had in his lime a cure for a great sanitary evil, but not knowing the effects, left it for a less valuable substance. I do not, however, propose lime as a bleacher of smoke, but as a remover of sulphur; and I think some mode of using this property may on inquiry be found. The mode of using it requires investigation, and many questions instantly suggest themselves. An inquiry by a public body would probably best find out the true mode of application, or bring to light a more efficient method.

XIX.—*Mineralogical Contributions.*

BY DR. HUGO MÜLLER.

I.—ON A METEORIC IRON FROM ZACATECAS IN MEXICO.

THE meteoric iron which forms the subject of this examination was brought some years ago from Zacatecas, where it was the property of the late Marchese Flores D'Arcais, who was Mining Director in those districts. It afterwards passed into the hands of Mr. Brice Wright of London, and I was induced to make an examination of it for the purpose of ascertaining whether this iron was identical with that formerly brought from the place mentioned or whether it ought to be considered as new. The label which accompanied the iron merely stated that it came from Zacatecas.

The piece from which the material for this examination was taken was of an irregular shape, it weighed about twenty pounds, and was evidently cut from a much larger mass, from which it probably projected. Those sides which, judging from the black crust, might have formed some part of the original surface, were irregularly impressed and rounded at the edges.

The iron is soft, tough, and difficult to break; the fractured surface shows a highly developed laminated structure. The polished surface contains irregular and circular spots, which are metallic, and of a dark bronze colour; when it is tarnished or etched there appear bright points, which are generally arranged in lines, intersecting each other in various directions. An oblique and intense illumination shows the intermixture of this bright substance throughout the mass of the iron.

The etched surface does not exhibit any Widmannstettian figures like the iron from Xiquipilco, Durango, and others coming from Mexico, but presents the crystalline appearance of tinned iron when subjected to the action of an acid (*moiré métallique*); resembling in this respect the meteoric iron formerly brought from Zacatecas, and analyzed by Bergemann.

The iron is not passive, and is dissolved with facility, even in diluted hydrochloric acid, when slightly warmed, leaving a small insoluble residue, which, however, dissolves entirely in aqua regia.

The dark bronze-coloured nodules imbedded in the iron likewise dissolve with great ease in dilute acids, with evolution of sulphuretted hydrogen, and behave in every respect like monosulphide of iron.

For the purpose of analysis, the iron was dissolved in a small tubulated retort with dilute hydrochloric acid, and the hydrogen disengaged was passed through a small bulb apparatus filled with nitrate of copper in order to absorb the sulphuretted hydrogen. The sulphur was finally determined as sulphate of baryta.

The solution of the iron was filtered off from the insoluble residue, and a copious stream of sulphuretted hydrogen passed through the liquid; this caused a yellow precipitate of sulphur containing a trace of copper. The solution was now oxidized with chlorate of potash, and in one case the iron was separated as succinate of iron; in another experiment it was precipitated by carbonate of baryta. In the former case, it was found that on washing the succinate of iron, a small quantity was dissolved, which fact was previously observed by W. Clark under similar circumstances, and appears to be due to the presence of phosphoric acid; for no solution took place in an experiment carried out in precisely the same way, excepting that the phosphoric acid had been previously removed.

The separation of phosphoric acid was effected by fusing the oxide of iron obtained with an excess of carbonate of soda and potash, and precipitating the phosphoric acid with sulphate of magnesia.

The use of succinic acid for separating the iron, necessitated the application of sulphide of ammonium for precipitating nickel, cobalt, and manganese, which operation, under circumstances not yet clearly made out, is rendered very difficult and troublesome on account of these metals, especially nickel and manganese, entering partly into solution. For this reason, the separation of the iron by means of carbonate of baryta is perhaps preferable. I have satisfied myself that iron can be perfectly separated in the latter way from nickel, cobalt, and manganese, if the proper precautions are taken.

Nickel and cobalt were separated according to the methods of Liebig, and also by precipitating the cobalt with carbonate of baryta, from the solution previously treated with chlorine or bromine.

The numbers obtained were as follows:—

- I. Analysis. 3.9393 iron gave 5.064 oxide of iron, 0.2987 oxide of nickel, 0.0314 oxide of cobalt, and 0.1215 insoluble residue. Phosphorus and silica not determined.
- II. Analysis. 4.1240 iron gave 5.377 oxide of iron, 0.3048 oxide of nickel, 0.0219 oxide of cobalt, 0.0374 pyrophosphate of magnesia, and 0.0907 insoluble residue. Sulphur and silica not determined.
- III. Analysis. 3.9315 iron gave 5.1042 oxide of iron, 0.2824 oxide of nickel, 0.0210 oxide of cobalt, 0.0327 pyrophosphate of magnesia, 0.0196 silica, 0.0210 sulphate of baryta, and 0.1070 insoluble residue.

The percentage corresponding to these numbers is:—

	I.	II.	III.
Iron . .	89.84	91.30	90.91
Nickel . .	5.96	5.82	5.65
Cobalt . .	0.62	0.41	0.42
Phosphorus	—	0.25	0.23
Sulphur . .	0.13	—	0.07
Silica . .	—	—	0.50
Copper . .	trace	trace	trace
Magnesia . .	trace	trace	trace
Insoluble residue	3.08	2.19	2.72
	<hr/> 99.63	<hr/> 99.97	<hr/> 100.50

For further examination of the residue which is left when the iron is dissolved in dilute hydrochloric acid, the whole quantity resulting from the different analyses was first subjected to a process of levigation, by which means a black flocculent substance was separated from a heavy shining body, which, under the microscope, did not show any defined form, but consisted of irregular pointed and flattened particles, of the colour of pure nickel, and possessing all the characteristic properties of Schreibersite. The lighter black flocculent, as well as the heavy and shining substance followed the magnet; and indeed by carefully applying the magnet, it was found that the whole of the original residue was magnetic. The black flocculent substance was present only

in very minute quantity, and could not be freed entirely from the Schreibersite. Believing it to be carbon or graphite in a fine state of division, I treated it with concentrated hydrochloric acid, in order to remove the admixture of Schreibersite; but to my great astonishment, it disappeared gradually, the vapours of the acid indicating the presence of sulphuretted hydrogen.

This result clearly shows that the black substance is not graphite nor any other form of carbon, but is most likely some sulphide, soluble only in concentrated hydrochloric acid.

Lastly, the heavy shining body was subjected to a quantitative analysis. It dissolved with facility in aqua regia slightly warmed, without leaving a trace of insoluble residue. The solution was mixed with excess of carbonate of soda and potash, evaporated to dryness and fused, in order to remove the phosphoric acid at once. The further operations of separating the other constituents, iron and nickel, were carried out in the manner above described.

0.5245 substance gave pyrophosphate of magnesium 0.2835.

0.5620 oxide of iron.

0.0965 oxide of nickel, corresponding to

Iron	.	.	.	75.02
Nickel	.	.	.	14.52
Phosphorus	.	.	.	10.23
				<hr/>
				99.77

This analysis furnishes an additional proof that the substance termed Schreibersite, and which forms a characteristic component of almost every meteoric iron, is of very variable composition; the quantities of iron, nickel, and phosphorus, which are the principal constituents, differ very materially in the Schreibersite of different kinds of meteoric iron.

Before concluding this account of my experiments, I must also mention that in one case the whole of the hydrogen given off on dissolving the iron in hydrochloric acid was passed through a tube filled with oxide of copper whilst in a state of ignition, and to this was attached an apparatus containing caustic baryta. This solution remained perfectly clear, and I therefore conclude that the hydrogen did not contain any carburetted hydrogen.

In another experiment, the hydrogen, after having been freed from sulphur by a solution of acetate of lead, was passed through a narrow glass tube, kept redhot during the whole operation. In

this case also, no deposit was formed which might indicate the presence of arsenic; nor could that element be detected in the pyrophosphate of magnesia obtained in the analysis of the iron.

Neither manganese nor chromium was found in this meteoric iron, and none of the minerals insoluble in acids which are sometimes met with in meteoric irons could be detected.

On comparing the results of this examination with those obtained by Bergemann in analyzing a meteoric iron which was formerly brought from Zacatecas,* it becomes evident that these meteorites are different. Even allowing for a discrepancy in the quantities of the constituents, which might vary with the irregularity in which the schreibersite, insoluble sulphides and sulphate of iron are distributed in the nickeliferous iron, the entire absence of carbon or graphite and chromic iron, which, according to Bergemann, amount to 0.49 for carbon and 1.48 for chromic iron, cannot be considered accidental.

The accompanying impression is a faithful representation of the appearance of an etched surface of this iron, and is obtained from a facsimile in electrotype. The straight lines indicate the arrangement of the particles of the Schreibersite, whilst the circular and lenticular dark spots represent the bronze-coloured sulphide of iron.

II.—ON A PECULIAR PSEUDOMORPH OF CINNABAR FROM POLA DE LENA IN ASTURIA, SPAIN.

Through the kindness of Mr. Mason, Mining Engineer of Bilbao, I obtained a specimen of cinnabar associated with realgar, which forms a principal produce of the Eugenia Mine, near Pola de Lena, in Asturia. The vein of this ore is situated in carboniferous limestone.

The specimen at my disposal consisted entirely of a mixture of realgar with cinnabar, the latter being irregularly intergrown with and imbedded in the realgar. A closer examination showed that the cinnabar formed distinct crystals of a considerable size, which became more apparent on removing the realgar by mechanical means, or by boiling with nitric acid, which readily

* W. S. Clark on Metallic Meteorites, page 28, J. pr. Chem. lxxi. page 59.



METEORIC IRON FROM ZACATECAS MEXICO.

dissolved the realgar. These crystals, however, are not of the form in which cinnabar crystallizes, but are tetrahedrons, perfectly developed, and not showing any modifications; they occur either as solitary individuals or clustered together in groups. Being induced by this peculiarity to examine the matter somewhat more closely, I first satisfied myself as to the composition of the crystals.

The material for analysis was heated in aqua regia, which readily dissolved it, leaving, however, a residue of sulphur. The solution was freed from nitric acid by boiling with hydrochloric acid; the separated sulphur was filtered off; and the sulphuric acid precipitated with chloride of barium. The mercury was precipitated by means of protochloride of tin.

2.3360 substance gave 1.9885 mercury, 0.1420 sulphur, 1.1075 sulphate of baryta, giving the percentage as follows:—

		Theory.
Mercury	. 85.12	86.2
Sulphur	. 14.35	13.8
	———	———
	99.47	100.0

This result agrees so nearly with the theoretic formula of cinnabar as at once to establish the identity.

Not being inclined to assume a dimorphism of cinnabar, I came to the conclusion that the crystals in question were pseudomorphous, and subsequently I had the satisfaction to find complete confirmation of this view amongst a larger quantity of these crystals removed from their matrix.

In the first place, I found that the cleavage, where it existed, was in no way connected with the external form; and, moreover, the silky lustre on the surface of the crystals was not at all in accordance with the faces of a tetrahedron; in the second place, I found a crystal of considerable size, which was incomplete on one corner, and there it showed how it was built up by the infiltration of cinnabar: the true form of the latter in minute crystals could be distinctly made out.

Taking this as sufficient proof for the pseudomorphous character of these crystals, the question arises as to what mineral the form is derived from. On this point, however, I cannot express any decided opinion. The fact that the smaller crystals, in particular, are so well developed, might suggest that fahlore was the original mineral, whilst some of the larger crystals in their mode of

clustering together resemble copper-pyrites. The difference of the angles of copper-pyrites and fahlore might serve to decide this question; however, unfortunately, the very small crystals do not possess sufficient brightness for a reflecting goniometer, whilst the faces of the larger crystals are not true enough planes to show an uniformity in the measurement of different crystals with a common goniometer.

The analysis of the realgar in which these pseudomorphs are imbedded furnished the following numbers:—

1.2725 substance gave 2.7825 sulphate of baryta, 2.2530 arseniate of ammonia and magnesia (2MgO , NH_4O , $\text{AsO}_5 + \text{HO}$; dried at 100°C), corresponding to:—

			Theory.
Sulphur	.	30.00	29.91
Arsenic	.	70.25	70.09
		<hr/>	<hr/>
		100.25	100.00

III.—LIBETHENITE FROM CONGO IN PORTUGUESE AFRICA.

Some distance inland from Loanda, near a place called Congo, there is situated a copper-mine of unusual richness, the principal ore of which is malachite. Through the kindness of Messrs. Pinto and Perez, I had an opportunity of looking over a large sample of the produce of this mine, brought to this country.

Amongst large lumps of pure and beautifully banded malachite, I found some pieces of a dark-olive colour and cellular structure, sprinkled over with small but brilliant crystals of the same colour. A closer examination of these crystals indicated a trimetric form, resembling that of olivenite and libethenite.

A perfect identity with the latter species was demonstrated by the following analysis.

This mineral being readily soluble in dilute nitric acid and also in ammonia, two analyses were made, using in one case nitric acid, in the other ammonia for the solvent. In both cases the copper was precipitated by sulphuretted hydrogen and the sulphide of copper converted into oxide. From the filtrate the phosphoric acid was separated in the usual way by means of sulphate of magnesia. Besides oxide of copper, phosphoric acid, and water,

no other element could be detected; the mineral is perfectly free from arsenic acid. The water was determined by loss.

I. Analysis. 1·6685 substance gave 1·1245 oxide of copper and 0·7465 pyrophosphate of magnesia.

II. Analysis. 1·2868 substance gave 0·8590 oxide of copper and 0·5840 pyrophosphate of magnesia.

Which numbers give the following percentage.

			Kühn found in Libethenite from Libethen
Oxide of copper	. 67·21	66·76	66·94
Phosphoric acid	. 28·76	29·02	29·44
Water 4·03	4·22	4·05
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·43

IV.—COLUMBITE FROM EVIGTOK, IN THE FIORD OF ARKSUT, IN GREENLAND.

This occurrence of Columbite was discovered a few years ago by Mr. J. W. Taylor, while engaged in the exploration of the mineral productions of West Greenland, and was mentioned by him in a highly interesting paper on the occurrence of Cryolite and its associates, communicated to the Geological Society of London.*

The columbite of this locality is remarkable for its well-developed and highly modified crystallization,† and is no doubt the most beautiful variety of this mineral yet found. It bears at first sight a considerable resemblance to certain specimens of tinstone, the crystals being either loose or clustered over pieces of decomposed feldspar and cryolite, or covering the sides of small cavities in the latter mineral.

The colour, when compared with that of the columbite of North America and Bodenmais, is lighter and more of a brownish black, not exhibiting the beautiful iridescence of the American columbite. Thin splinters transmit the light with a dark reddish brown colour; the streak is chocolate brown.

The crystals generally are intergrown (*eingewachsen*) with small

* Journal Geological Society, vol. xii. Part I. page 140.

† Descloizeaux. Ann. des Mines.

crystals of feldspar (albite?), galena, and molybdenum, and when broken, frequently show concentric rings, which are produced by intersected layers of a siliceous mineral. It therefore becomes more difficult, than would appear from the external appearance of the crystals, to obtain by mechanical means only, material of this columbite pure enough for analysis.

On treating, however, the coarsely powdered mineral with cold hydrofluoric acid, and subsequently with boiling nitric acid, every visible trace of foreign matter can be completely removed.

Warm hydrofluoric acid dissolves the columbite entirely.

The specific gravity of the purified columbite was found to be 5.40 — 5.42.

The analysis was carried out in the usual way by fusing the finely powdered mineral with bisulphate of potash, treating the resulting sulphate of columbic acid with sulphide of ammonium, for the purpose of separating a trace of tin, and lastly, igniting the columbic acid with carbonate of ammonia, to remove any trace of sulphuric acid.

3.0540 substance gave 2.4048 columbic acid (niobic acid),
 0.5650 oxide of iron,
 0.1682 sesquioxide of manganese,
 0.0050 oxide of tin (containing tungstic acid),

which numbers give the following percentage:—

Columbic acid (niobic acid)	=	78.74	78.56	79.0
Protoxide of iron . . .	=	16.40		
Protoxide of manganese	=	5.12		
Oxide of tin and tungstic acid	=	0.16		
		<hr/>		
		100.42		

neither magnesia nor lime could be detected.

In two other experiments, 78.56 and 79.0 of the metallic acid were obtained.

It will be seen from this analysis that the composition of this columbite is almost identical with that of Middletown, U. S.*

* I take this opportunity to correct a typographical error which entered into the original publication of the analysis of Columbite from Tirschenreuth, in Bavaria, which I made some years ago. It should be:

Columbic acid 78.6, protoxide of iron 15.1, protoxide of manganese 5.2, oxide of tin 0.17.

This analysis was made two years ago, just about the time when the paper of Hermann* appeared, in which he stated that the columbite of Bodenmais contains tantalic acid. As he also gives a mode of effecting the separation of this acid, I made some experiments with the acids of this columbite to ascertain the absence or presence of tantalic acid. I was unsuccessful in obtaining any definite result; nor could I succeed in making out any two different acids in the columbite of Bodenmais in the way indicated by that chemist. In the meantime T. Oesten † has taken up this subject, and more fully entered into it; he likewise did not succeed in separating tantalic acid from any of the true columbites; and he altogether denies the possibility of separating tantalic acid from the acid of the columbites in the way described by Hermann.

In conclusion, I offer my best thanks to Mr. Warren De La Rue, in whose laboratory these analyses were carried out.

XX.—Contributions to the knowledge of the Amyl group.

By FREDERICK GUTHRIE.

I.—NITRITE OF AMYL AND ITS DERIVATIVES.

Nitrite of Amyl.— $C_{10}H_{11}O, NO_3$.—As this body was made the starting point from which certain new compounds were formed, and as it belongs to a very interesting group of bodies which have not been much studied, I shall, in the first place, describe some of its properties which have hitherto remained unnoticed.

Nitrite of amyl, when perfectly dry, boils at $99^{\circ}C$. in a glass vessel, in contact with platinum wire, under a pressure of 756^{mm} . A small quantity of moisture depresses the boiling point two or three degrees, apparently by diminishing the cohesion of the liquid.

As a solvent, nitrite of amyl may be placed between oxide of ethyl and bisulphide of carbon. It is miscible in all proportions with these liquids, as also with the alcohols and ethers both single and double, with benzol, paraffin, naphthalin, and the hydrocarbons. It dissolves abundantly the fats, oils and fatty acids, and disintegrates gutta-percha and caoutchouc. Sulphur and

* J. pr. Chem. lxxiii. 65.

† Pogg. Ann. ciii. 184.

phosphorus are dissolved sparingly; gun-cotton at ordinary temperatures and pressures remains unaffected by it.

One of the most prominent of its properties is the singular effect of its vapour, when inhaled, upon the action of the heart. If a piece of bibulous paper, moistened with two drops of the nitrite of amyl, be held to the nostrils, through which the breath is exclusively drawn, after the lapse of about fifty seconds, a sudden throbbing of the arteries of the neck is felt, immediately followed by a flushing of the neck, temples and forehead, and an acceleration in the action of the heart. These symptoms last for about a minute and then cease as suddenly as they began. By inhaling the vapour from the above quantity, the pulsation of the heart may be raised from 70 to 140 per minute, even when absolute rest is observed. The acceleration becomes painful if the inhalation be accompanied with, or immediately preceded by, violent muscular exertion. The effect is still more marked, if, the nostrils being held closed, the same quantity is dropped upon the back of the tongue, and the breath drawn deeply over it. To ascertain the effect of a larger quantity, a piece of cotton-wool was moistened with about twenty drops, and being placed in a paper cone, was held over the mouth and nostrils of a rabbit. The animal did not offer any resistance. On removing the cone after five minutes, no signs of uneasiness were observed until twenty minutes had elapsed, when the rabbit sprang up and, after running about for a few seconds, lay down on its stomach, stretching out its legs. The protrusion of its eyes and its cries showed that it suffered pain. The power of voluntary motion seemed almost suspended, especially on the left side, both the left legs being either insensible to pain or incapable of motion.

The animal appeared to have recovered completely in a quarter of an hour after the first symptom. Even when diluted with large quantities of air, the vapour of nitrite of amyl has a very unpleasant effect upon the head if breathed for a long time; but beyond a very slight tendency to headache, seems to be without any subsequent injurious effect.*

Two points are worthy of note in the above experiments; firstly,

* It may be proper to recall the fact observed by Hofmann, that crude nitrite of amyl, as prepared by the action of nitrous acid upon amyl alcohol, contains hydrocyanic acid; this must of course be removed by caustic soda before experiments such as the above can be tried. The presence of this impurity was probably the cause of its discoverer, Balard, attributing to nitrite of amyl the power of producing violent headache. No such effect was experienced by the fifteen or twenty students, of ages varying from fifteen to twenty-five, whom I have induced to try it.

that the vapour of the nitrite of amyl has a different effect from that of its analogue in the ethyl series, nitrite of ethyl, the active constituent of sweet spirits of nitre, having rather an opposite or soothing effect. Secondly, that the time required to attain the maximum effect differs in the cases of the human subject and the rabbit ;—the former, as mentioned, occurring in fifty seconds, the latter in twenty minutes.*

If a few drops of nitrite of amyl be heated in a flask till their ebullition has expelled all the air, and the heat be still applied after all the liquid has disappeared, a slight detonation occurs, accompanied by the livid flame of burning nitrogen compounds. This is doubtless due to the partial combustion of the vapour of the body at the expense of its own oxygen. To determine the precise temperature at which this decomposition occurs, a bath of fusible metal with inserted thermometer was gradually heated, and the nitrite of amyl allowed to drop upon it at regular intervals of such magnitude that the disturbance of temperature due to its evaporation might be supposed unimportant. As soon as the liquid took fire on coming into contact with the heated metal, the temperature was alternately depressed and elevated through the observed point. In this way the temperature 260°C . was found to be, within a few degrees, that necessary and sufficient to determine the combustion. Spongy platinum placed upon the surface seemed to exercise no influence upon the temperature required to effect the decomposition.

Action of nascent Hydrogen.—It was to be expected that a body holding somewhat loosely a highly oxidized group, the latter being itself of unstable character, would undergo some change in the presence of nascent hydrogen. Into a flask provided with a funnel and exit-tube and containing three ounces of granulated zinc, an ounce of the nitrite of amyl was introduced ; to this three ounces of alcohol at 50°B . were added, and then a mixture of equal parts of sulphuric acid and water allowed to enter slowly. The exit-tube was brought into a flask surrounded by a freezing mixture and the decomposition flask was immersed in cold water. When the zinc was nearly dissolved, the apparatus was disconnected. On adding water to the contents of the decomposition flask, an oily liquid, lighter than water, was separated, which on drying and rectifying gave a product boiling at 132°C . Burnt with oxide of copper, 0.3432 of this gave 0.8602 of carbonic acid and 0.4312 water.

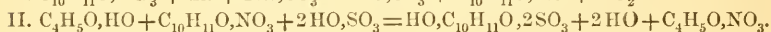
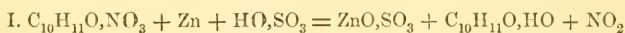
* It is probable that this body may find an application in medicine as a resuscitative, as in cases of suffocation, drowning or protracted fainting.

		Calculated.	Found.
C ₁₀	..	68·18	68·36
H ₁₂	..	13·64	13·96
O ₂			

It was therefore amylic alcohol. The aqueous solution from which it separated was evaporated to dryness with metallic zinc. The dry mass was shown to contain mere traces of organic matter, it consisted essentially of sulphate of zinc and sulphate of ammonia. The contents of the artificially cooled flask boiled on the application of the heat of the hand. It was distilled from a water bath at 40°. 0·3415^{gram} gave on analysis 0·4606 carbonic acid, and 0·2168 water.

		Calculated.	Found.
C ₄	..	32·00	36·78
H ₅	..	6·66	7·05
N			
O ₄			

being therefore nitrite of ethyl containing alcohol. It has all the physical properties of such a liquid, and on boiling with alcoholic solution of caustic potash, yields nitrite of potash and a liquid wholly miscible with water. There are, therefore, in the first place, two simultaneous recompositions; the one, the formation of the amylic alcohol, being due to the action of the nascent hydrogen; the other, the formation of the nitrite of ethyl, being caused by the reaction upon the ethylic alcohol of the nitrous acid, as it is driven out of combination by the mineral acid employed.



But neither reaction stops here: the nitric oxide of the first is hydrogenated to ammonia, and the amylosulphuric acid of the second is decomposed as soon as formed. The above two curious reactions are of course independent of one another and the latter may be almost entirely prevented by using very dilute sulphuric acid. It is noteworthy, in the above reaction, that a body, nitrite of ethyl, is formed which is decomposable in alcoholic solution by sulphuric acid. That it nevertheless escapes decomposition is evidently owing to its volatility, by virtue of which it is removed as soon as formed from the field of chemical change.

Metallic Potassium effects an analogous reaction as far as the formation of amylic alcohol is concerned.

Action of Chlorine.—On passing pure and dry chlorine through

nitrite of amyl in an inverted retort connected with a condenser, heat was evolved and hydrochloric acid liberated, the contents of the retort changing in colour in succession from pale yellow to ruby red, olive green, and finally to pale, almost invisible green. The action was stopped at this point and a portion of the liquid being warmed and filtered to remove a small quantity of chloride of ammonium which separated out, was analysed. 0.2920gm. gave 0.0930gm. chloride of silver, 0.2039gm. gave 0.0707gm. chloride of silver. The two portions were from two separate preparations; the first contained accordingly 7.90 and the second 8.60 *per cent.* of chlorine. These numbers correspond most nearly with a substitution of one atom of chlorine for hydrogen in three atoms of the nitrite. This body has the specific gravity 0.909, but it is probably a mixture of the body next to be described, with undecomposed nitrite of amyl. If the current of chlorine be continued through the above liquid and its action be assisted by the heat of a water-bath, further evolution of hydrochloric acid results. When this has ceased, and the liquid and exit tubes show the presence of free chlorine, the action, as far at least as it goes in diffused daylight is complete. The contents of the retort are then shaken up with mercury and dilute ammonia to remove the excess of chlorine and hydrochloric acid, and dried over sulphuric acid in *vacuo*. 0.4561gms. gave 0.6109gms. carbonic acid and 0.2436gms. water. 0.2633gms. gave 0.3875gms. chloride of silver. The liquid has therefore the composition :—

		Calculated.	Found.
C ₁₀	.. 60	32.26	36.53
H ₉	.. 9	4.84	5.93
Cl ₂	.. 71	38.20	36.39
N			
O ₄			

The above numbers show that the replacement was not quite complete; the substance analysed had been exposed for two hours to a rapid current of chlorine. This body is the *nitrite of bichloramyl*, $\left. \begin{matrix} \text{C}_{10} \text{H}_9 \\ \text{Cl}_2 \end{matrix} \right\} \text{O,NO}_3$: that is, the nitrite of amyl wherein two atoms of hydrogen are replaced by chlorine. Nitrite of bichloramyl is a transparent colourless liquid of peculiar pine-apple odour, and very bitter and persistent taste. It is non-miscible with, and undecomposed by water: its specific gravity at 12°C. is

1.2333.* It is not volatile without partial decomposition. On distillation it begins to boil at 90°C. The boiling point rises to 200°C.: when this temperature is reached, the distillate is colourless, the residue black. Both are heavier than, non-miscible with, and undecomposed by, water.

Action of Phosphorus.—In the cold or at temperatures just sufficient to melt phosphorus, nitrite of amyl, as mentioned above, acts as a solvent. But at a temperature above this and below the boiling point of the nitrite, a true chemical action commences, the basis of which is the oxidation of the phosphorus at the expense of the oxygen of the organic nitrite. When the action has once commenced, which is seen by the evolution of a permanent gas, sufficient heat is evolved to carry it on without the application of external heat. If some ounces of the nitrite be employed, the temperature towards the end rises to 121°C., soon after which the action ceases abruptly. In order to trace this reaction, weighed quantities of nitrite of amyl and of phosphorus were employed, and the evolved gas was passed through two bulb wash-tubes, the first containing alcohol and the second water, and then through a chloride of calcium tube. The three tubes were all weighed. The flask containing the phosphorus and the nitrite was immersed in a water-bath, the temperature of which was so regulated as to effect a regular disengagement of gas. When the reaction was finished, the residual phosphorus, the liquid residue in the flask, and the three tubes, were again weighed. In an experiment of this kind, after making the proper corrections, it was found that 18.53gms. of nitrite of amyl were acted on by 2.00gms. of phosphorus. As 16.00gms. of residual liquid remained in the flask, it follows that 4.53gms. of gas had been evolved; but as the gas so formed still contained organic matter, the latter number is probably somewhat too high. The gas was collected over mercury, and washed first with alcohol, then with water. The portion first collected contained about 70 per cent. of nitrogen, 4 per cent. of nitric oxide,

* The following simple device may be sometimes conveniently employed in determining the specific gravity of small quantities of liquids which are neither miscible with, nor decomposed by water, and whose specific gravities do not greatly exceed unity (say from 1 to 2). A single drop of the liquid to be examined is brought into a tall cylinder glass containing a little water, and immersed in a large beaker glass. A strong clear solution of chloride of calcium is added in small quantities at a time, care being taken not to break the drop of the liquid being examined, and to allow the solution to regain the temperature of the surrounding water. When such quantity has been added that the drop is in indifferent equilibrium, the specific gravity of the chloride of calcium solution is taken in the ordinary way with the specific gravity bottle, and it is of course identical with that of the liquid under examination.

and 26 of nitrous oxide: the latter portions were richer in nitrous oxide.* The reaction is therefore not a simple one. In two other experiments, in which the gas was not passed through wash-tubes, 1 part by weight of phosphorus gave rise to 8, and to 6·7 of residual liquid respectively.

The residual liquid was exposed to the air for several weeks to oxidize the free phosphorus which it held in solution, then heated to 150° to expel any unchanged nitrite of amyl, and finally repeatedly dissolved in alcohol and reprecipitated by water and dried in *vacuo* over sulphuric acid. Thus purified, a light brown oily liquid is obtained, which is quite insoluble in, and undecomposed by, water. Its specific gravity at 20°C. is 1·02; but it expands more rapidly than water, and at 70°C. has the specific gravity 1.

On analysis it showed the following composition:—

·5470 ^{gm.}	gave	·9598 ^{gm.}	carbonic acid and	·4458 ^{gm.}	water
·4676 ^{gm.}	gave	·8102 ^{gm.}	carbonic acid and	·3885 ^{gm.}	water
·4702 ^{gm.}	gave	·1989 ^{gm.}	pyrophosphate of	magnesia	
·1947 ^{gm.}	gave	·0116 ^{gm.}	nitrogen.		

These numbers agree best with the formula $C_{20}H_{23}PNO_8$.

	Calculated.		Found.	
C_{20} ..	47·61	47·25	47·86	—
H_{23} ..	9·12	9·19	9·06	—
P ..	12·30	—	—	12·08
N ..	5·55	—	—	—
O_8 ..	25·43			6·0

It is difficult to see what the rational formula of this body should be. Until some further light be thrown upon it, it may be called *amylonitro phosphorous acid*. It may be heated to 160°C. without decomposition; above this temperature it blackens and gives off hydride of amyl.

Amylo-nitrophosphite of potash is prepared by digesting the acid with alcoholic solution of caustic potash, passing carbonic acid through to neutralize the excess of potash, digesting with alcohol, filtering and evaporating. Dried in *vacuo* over sulphuric acid, it is a yellowish, finally granular, highly deliquescent body, soluble in water and alcohol. Dilute mineral acids separate out the

* The presence of nitrous oxide enabled me to determine the nitric oxide by combustion with hydride.

organic acid in heavy drops. Heated by itself it swells up and finally deflagrates.

The baryta, silver, lead, and copper salts are prepared from the potash salt on adding a soluble salt of the respective bases. They are all precipitated at first as light, flocculent, amorphous bodies. On agitating or warming them, they adhere together, forming tenacious gummy substances, which become dry and brittle under the air-pump. The silver salt cannot be dried without partial decomposition. Analysis showed all the above salts to be bibasic, with the exception of the lead salt, which gave discordant results on analysis, and whose composition is therefore doubtful. The acid is separated from all its salts on the addition of sulphuric or hydrochloric acid.

XXI.—*On Ammonia and its Derivatives.*

A Discourse delivered to the Members of the Chemical Society of London.

BY PROFESSOR HOFMANN.

(June 17, 1858.)

THE labours of inquirers in the field of Organic Chemistry, during the last ten years, have been marked by the attempt to refer the constitution of the numerous vegetal and animal substances and of their artificial derivatives to a comparatively small number of forms, the prototypes of which, such as *sea-salt*, *water*, and *ammonia*, are to be found in Mineral Chemistry. With the majority of substances, Chemists have been more or less successful, but the constitution of a great number of bodies remains doubtful, their type remains as yet uncertain; in many this type is altogether unknown.

Among the several typical classes into which organic compounds are thus divided, the ammonia-group stands foremost for its richness, the diversity of its members, the number of connecting links which establish a passage from the ammonia-type to other types, and lastly, for the remarkable extent and precision which characterise our knowledge of most of its members. The derivatives of ammonia include within their ranks substances of

the most opposite chemical, physical, and physiological characters,—well-defined acids, neutral bodies, and the endless variety of artificial and natural organic bases;—they are capable of becoming, by the simple accession of the elements of water, or by the assimilation of acids, representatives of the water-type, or of the chloride-of-sodium-type;—and lastly, they are intimately connected with a numerous group of analogous bodies, containing phosphorus, arsenic, and antimony. Thus, the ammonia-derivatives ramify into the most interesting parts of chemical science, the progress of which is inseparably linked with their history.

In the following remarks, I propose to take a survey of the chemistry of ammonia; but owing to the almost boundless extent of the field over which I shall have to travel in a comparatively short time, I must limit myself to a rapid sketch of the most prominent features of the ground. Losing sight altogether of the physical characters of the ammonia-derivatives, and avoiding all details of their preparation, I shall endeavour to classify them in accordance with the present aspect of science, and to show the relation in which they stand to their prototype, alluding at the same time briefly to the sources from which they are obtained.

The unusually great number of the derivatives of ammonia is chiefly due to the peculiar construction of this body. Chemists unanimously agree in assuming that the molecule of ammonia contains one molecule of nitrogen and three molecules of hydrogen. Of these three molecules of hydrogen, one, two, or three may be replaced by other molecules, simple or compound. This circumstance alone must raise the number of bodies belonging to the ammonia-type far above that of any other class of substances. But experiment has proved that, under the influence of agents apt to replace more or less hydrogen, two, three, four, and probably even five molecules of ammonia, are capable of coalescing into molecules of a higher order, in which two, three,—twelve, or perhaps, even fifteen molecules of hydrogen are now found to be exchangeable for other molecules. Again, the analogues of ammonia in the phosphorus-, arsenic-, and antimony-series, (phosphoretted, arsenetted, and antimonetted hydrogen),—bodies whose constitution is exactly similar to that of ammonia,—furnish each a number of derivatives not inferior probably to those of ammonia itself, which, in the general conception of the question, cannot be separated from ammonia. Under special circumstances, ammonia seems to have the power of associating with its phosphoretted,

arsenetted, and antimonetted analogues, so as to form molecules of a higher order, containing simultaneously nitrogen and phosphorus, nitrogen and arsenic, nitrogen and antimony, perhaps even three or four of these elements. It is obvious that here are the conditions for the formation of a group of compounds, the number and variety of which are beyond the boldest imagination.

The derivatives of ammonia may be at once divided into two large groups, namely :

A. Bodies in which the chemical character of ammonia is preserved, and

B. Bodies in which the chemical character of ammonia has become extinct.

The first class embraces that large number of compounds known as organic bases, many of which are elaborated in animals and plants (animal and vegetal alkaloids), whilst the greater number are produced in the laboratory (artificial bases). This class is often designated by the general term *Amines*, which may again be subdivided into *Monamines*, *Diamines*, *Triamines*, *Tetramines*, etc., according as they are derived from 1, 2, 3, or 4 molecules of ammonia. The second class consists of neutral bodies, mostly produced by artificial processes, comparatively few terms of this group having been met with in the animal or vegetal organism. They are distinguished by the general designation *Amides*, and may be similarly subdivided into *Monamides*, *Diamides*, *Triamides*, *Tetramides*, etc.

A. AMINES.	B. AMIDES.
a. <i>Monamines</i> .	a. <i>Monamides</i> .
b. <i>Diamines</i> .	b. <i>Diamides</i> .
c. <i>Triamines</i> .	c. <i>Triamides</i> .
d. <i>Tetramines</i> .	d. <i>Tetramides</i> .

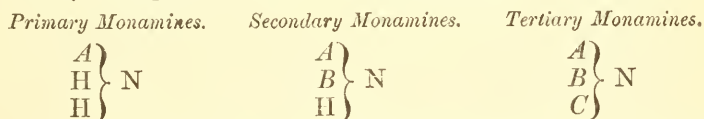
This classification, although far from embracing every individual member of the host of ammonia-derivatives, either known or conceivable, may nevertheless serve as a thread to guide us through the intricacies of this labyrinth.

A. AMINES.

a. *Monamines*.

By this term we designate a very numerous class of bodies derived from one molecule of ammonia, bodies in which the basic character of this substance, its power of combining with acids, is

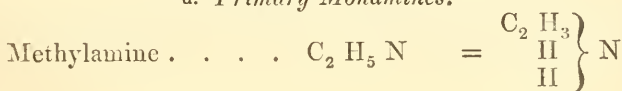
preserved. Some of these bodies are found in nature; but the majority have been obtained by artificial processes, some of which are of very general applicability, and admit of producing an almost unlimited number and variety of this class of substances. The monamines may be again classed into three sub-divisions, according to the number of hydrogen-equivalents in the ammonia-molecule, which are replaced. We distinguish—*a. Primary Monamines*, derived from one molecule of ammonia by the substitution of a radical for 1 equiv. of hydrogen; *β. Secondary Monamines*, by the substitution of radicals for 2 equivs. of hydrogen; and *γ. Tertiary Monamines*, derived from ammonia by the substitution of radicals for the 3 equivs. of hydrogen. These three subdivisions may be represented by the following general formulæ:



All the terms belonging to these three groups are true ammonias. They combine with the hydrogen-acids, and with the so-called hydrated oxygen-acids without elimination of water, forming saline bodies, generally of well-defined character. Their hydrochlorates yield, with bichloride of platinum, with terchloride of gold, with chloride of mercury, and many other chlorides, a series of very characteristic salts, which have often been studied with the view of fixing the nature of the organic constituent. Nearly all the monamines are volatile, their boiling points being lower or higher according to the number of hydrogen-equivalents replaced, and according to the nature of the compound molecules by which the substitution is effected. Nearly all these bodies are characterised by a peculiar odour, frequently resembling the odour of ammonia, but likewise considerably modified by the degree and nature of the substitution. Most of these bodies, when in contact with water, exhibit the alkaline reaction of ammonia, which is however considerably diminished in some, and altogether lost in others.

In the following tables we have united some of the most interesting terms of the three classes of monamines:

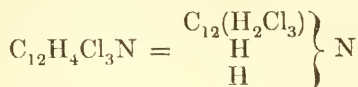
a. Primary Monamines.



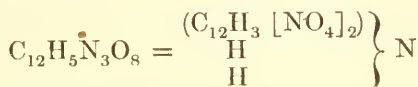
Ethylamine	$C_4 H_7 N$	$=$	$\left. \begin{array}{c} C_4 H_5 \\ H \\ H \end{array} \right\} N$
Amylamine	$C_{10} H_{13} N$	$=$	$\left. \begin{array}{c} C_{10} H_{11} \\ H \\ H \end{array} \right\} N$
Allylamine. . . .	$C_6 H_7 N$	$=$	$\left. \begin{array}{c} C_6 H_5 \\ H \\ H \end{array} \right\} N$
Phenylamine (Aniline) .	$C_{12} H_7 N$	$=$	$\left. \begin{array}{c} C_{12} H_5 \\ H \\ H \end{array} \right\} N$
Chlorphenylamine . .	$C_{12} H_6 Cl N$	$=$	$\left. \begin{array}{c} C_{12} (H_4 Cl) \\ H \\ H \end{array} \right\} N$
Dichlorphenylamine .	$C_{12} H_5 Cl_2 N$	$=$	$\left. \begin{array}{c} C_{12} (H_3 Cl_2) \\ H \\ H \end{array} \right\} N$
Nitrophenylamine . .	$C_{12} H_6 N_2 O_4$	$=$	$\left. \begin{array}{c} C_{12} (H_4, NO_4) \\ H \\ H \end{array} \right\} N$
Tolylamine (Toluidine)	$C_{14} H_9 N$	$=$	$\left. \begin{array}{c} C_{14} H_7 \\ H \\ H \end{array} \right\} N$
Naphtylamine . . .	$C_{20} H_9 N$	$=$	$\left. \begin{array}{c} C_{20} H_7 \\ H \\ H \end{array} \right\} N$

A glance at this table shows that the molecules replacing the hydrogen in ammonia are chiefly hydrocarbons; we meet, almost exclusively, with radicals of well-established alcohols, partly fatty, partly aromatic. The hydrogen of these radicals may be partly exchanged for chlorine, bromine, iodine, and the elements of hyponitric acid, as seen in chlorphenylamine, dichlorphenylamine, and nitrophenylamine; but the basic character of these secondary substitution-products is always considerably impaired. Chlorphenylamine is a much weaker base than phenylamine;

the saline compounds of dichlorophenylamine undergo decomposition even by water, whilst trichlorophenylamine

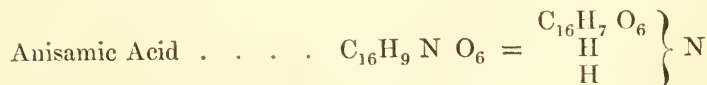
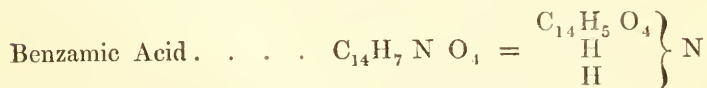
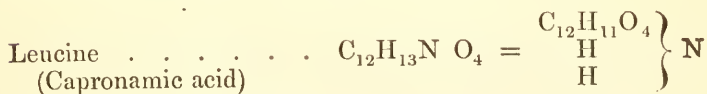
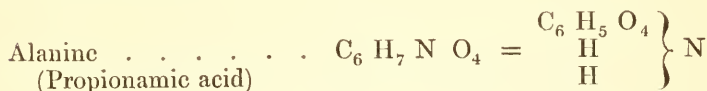
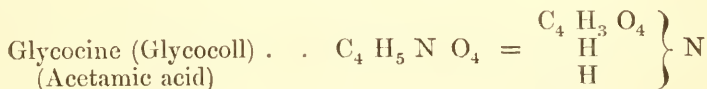


is no longer capable of combining with acids. In a similar manner, nitrophenylamine is much weaker than phenylamine; and dinitrophenylamine

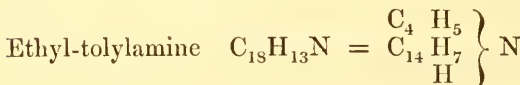
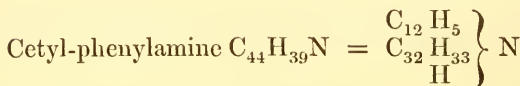
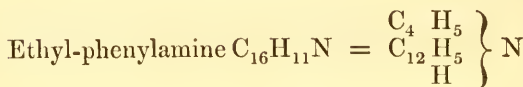
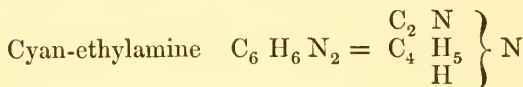
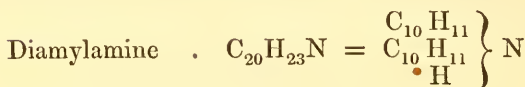
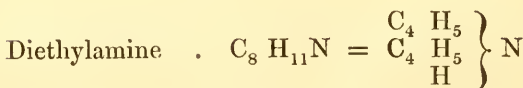
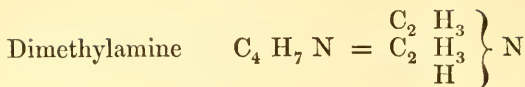


is a perfectly neutral body.

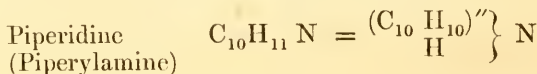
In some of the monamines, the replacing molecules are oxygenated. As illustrations, the following substances may be quoted:



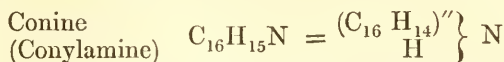
In the primary monamines of this description, the basic character is very feebly developed. In fact, these bodies are intermediate between acids and bases; in many of them, such as benzamic and anisamic acids, the basic nature has been only recently established.

β. Secondary Monamines.

The group of secondary monamines embraces several bodies, the constitution of which is not so clear as that of the substances given in the preceding table. By a method which will be more fully discussed hereafter, it has been experimentally demonstrated that piperidine is a secondary monamine; but we are unacquainted with the nature of the radicals which are substituted for the 2 equivs. of hydrogen; we even do not know whether these 2 equivs. of hydrogen are replaced by 2 monatomic radicals, or by one molecule of diatomic substitution-power. The latter view is, in fact, the simpler one; we therefore assume in piperidine a diatomic radical $\text{C}_{10}\text{H}_{10}$ (piperyl), and adopt, until further researches have thrown additional light upon this substance, the formula—

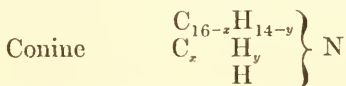
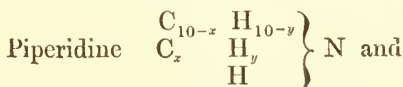


A perfectly similar remark applies to conine, the base obtained from *conium maculatum*.



Here again the nature of the complex molecule, equivalent to H_2 , is not established. The assumption of a diatomic molecule $\text{C}_{16}\text{H}_{14}$, is not supported by analogy. With greater probability we surmise the presence of 2 equivs. of a monatomic molecule C_8H_7 , perhaps butyryl. It is well known that, under the influence of oxidizing agents, conine is readily converted into butyric acid.

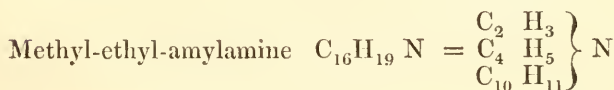
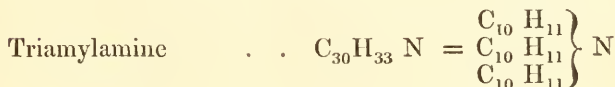
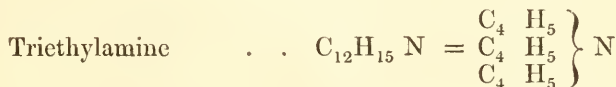
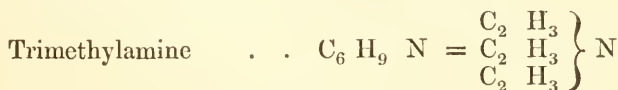
Further experiments, however, are required to establish finally the constitution of piperidine and conine; and as long as they are wanting, the constitution of these bases is perhaps better represented by the formulæ :

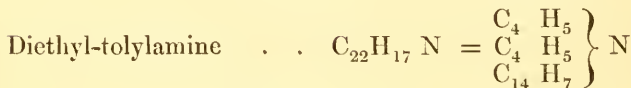
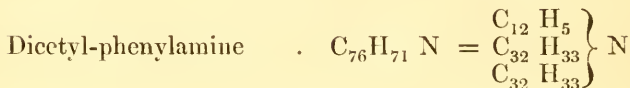
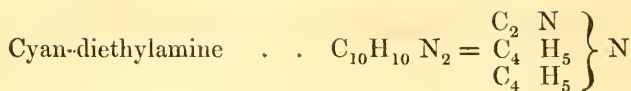


which include no hypothesis whatever.

γ. Tertiary Monamines.

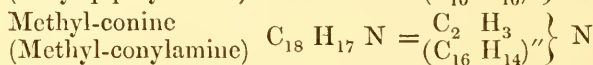
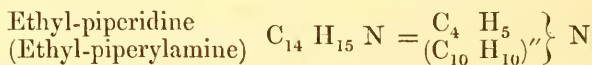
This group is very largely represented, for it embraces not only a considerable number of artificial bases, but likewise a great many vegetal alkaloids. The following are all artificial.



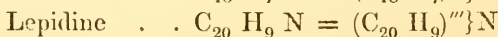
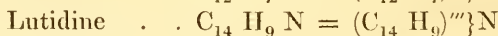
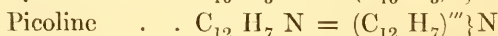
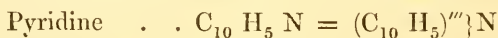


Closely connected with the substances given in this table is a series of bases in which the character of tertiary monamines is well established, although in other respects their constitution remains still doubtful.

Piperidine and conine have been enumerated among the secondary monamines. If the remaining equivalent of hydrogen in these bases be replaced by radicals, we arrive at monamines, the tertiary character of which cannot be doubted, however imperfectly we may be acquainted with the replacing radicals.

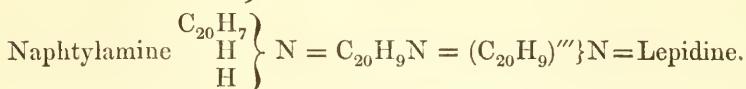
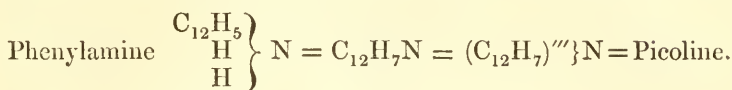


A considerable number of bases separated from the distillation-products of coal, of animal matters, in general of nitrogenous bodies, deserve next to be mentioned. All these bases are derived from one molecule of ammonia; we know that the 3 equivalents of hydrogen in the ammonia-molecule of these substances are replaced; but we have at present no facts at our disposal which would enable us to form an idea regarding the arrangement of the carbon and hydrogen in the replacing radicals.



A glance at these formulæ at once explains the frequent occur-

rences of isomeric ammonia-derivatives. Phenylamine, and picoline are isomeric, as also are naphtylamine and lepidine. But how different is the constitution of these bodies !

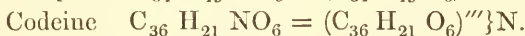
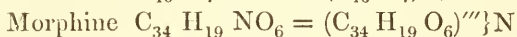


Phenylamine and naphtylamine are well defined primary monamines, whilst picoline and lepidine belong to the tertiary monamines, whatever the molecular arrangement of C_{12}H_7 or C_{20}H_9 may be. Whether each of these carbo-hydrogen-groups represents one triatomic molecule, or a diatomic, together with a monatomic one, or, lastly, three monatomic molecules,—we know that their sum is equivalent to 3 eqivs. of hydrogen.

Among the tertiary monamines, a group of artificial sulphuretted bases must be quoted, of which thialdine may be considered as the type.



In the same class, lastly, occurs a number of vegetal alcaloids, of which nicotine, morphine, and codeine are prominent terms.

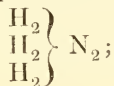


It has been already pointed out that, under the influence of polyatomic radicals, several ammonia-molecules are capable of associating so as to form ammonias of a higher order. They are often designated as polyammonias, which are again subdivided into polyamines and polyamides, according to the chemical character exhibited by the new compounds.

It may at once be stated that the group of polyamines is rather limited when compared with the numerous representatives of the class of monamines. The polyamines at present known, with very few exceptions, are—

b. Diamines.

The ideal type of this group is diammonia—



and, exactly as among the monamines, we might again distinguish—

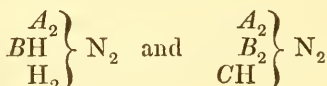
Primary Diamines,

Secondary Diamines, and

Tertiary Diamines.



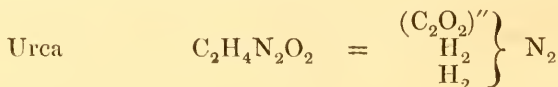
But it is obvious that this group embraces several other classes, for we readily conceive the existence of intermediate compounds :

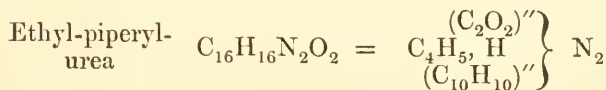
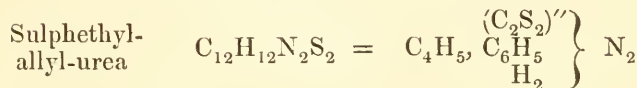
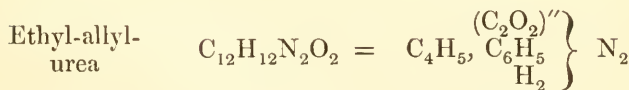
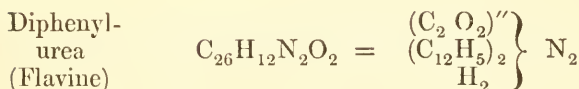
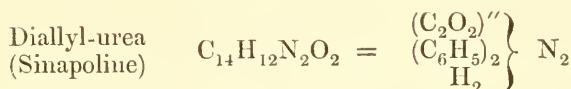
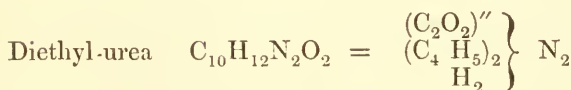
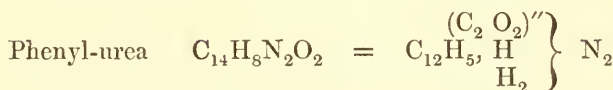
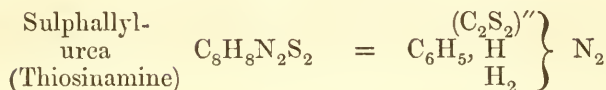
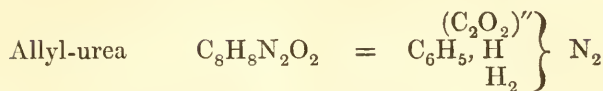
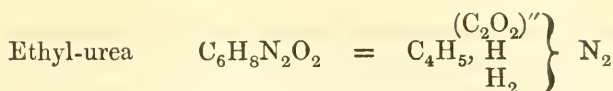


Even the number and nature of the radicals, by which the work of substitution is performed, suggest additional sub-divisions; for we may assume molecules of monatomic, diatomic, triatomic, and even tetratomic substitution-power involved in the formation of the diamines. Lastly, a broad line of demarcation appears in the chemical character of these bodies; for while in some of them the saturating power increases with the number of ammonia-molecules which are linked together,—some of the diamines combining with 2 equivs. of acid,—we find that the majority, in their relation to acids,—imitate the deportment of the monamines. It is obvious that the question, whether a diamine is capable of uniting with 1 or 2 equivs. of acid, must be intimately connected with the molecular construction of the basic system. As yet, this connection remains unknown, and we are surprised to find this difference of saturating power in diammonic compounds which, in every other respect, exhibit the greatest analogy.

One of the most interesting groups of diamines is furnished by the bodies generally designated as *Ureas*, and of which urea, *par excellence*, furnishes the well known prototype. There are few bodies the constitution of which has elicited a greater variety of views than that of urea. Most simply, urea appears as a diamine produced by the substitution of the diatomic radical carbonyl (C_2O_2)'' for 2 equivs. of hydrogen in diammonia. The formation, chemical character, and products of decomposition of urea, are in perfect accordance with this view.

In the following table we give some of the more interesting ureas :—

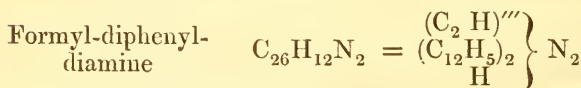
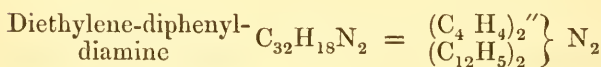
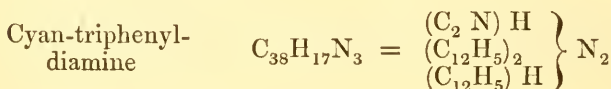
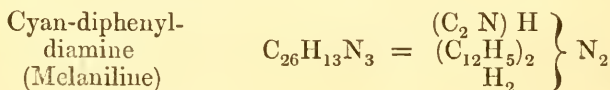




A glance at this table shows that in the formation of the ureas 2, 3, 4 and 5 equivs. of hydrogen in diammonia are replaced by compound molecules, and we shall see further on that it is pos-

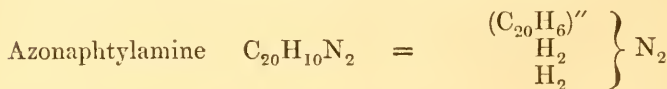
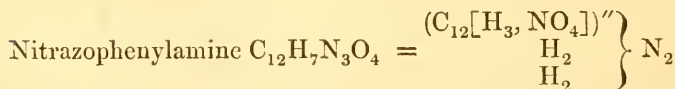
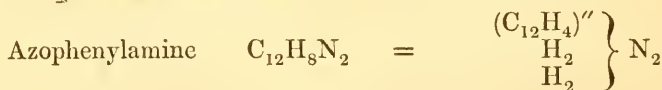
sible even to produce ureas in which unreplaced hydrogen no longer exists. The replacing molecules are the same as those involved in the transformation of ammonia into monamines. All the ureas are monacid with the exception of diphenyl-urea (flavine) which is a diacid base.

A less numerous, though not less defined, class of diamines are found among the derivatives of phenylamine and its homologues. The following formulæ exhibit the diversity of constitution of these bodies which are generated by a great variety of reactions:—



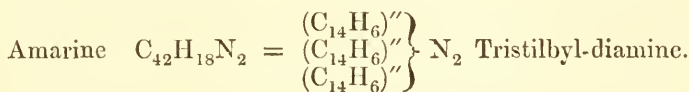
All these diamines are monacid with the exception of diethylene-diphenyl-diamine, which is diacid.

The construction of the class of diamines of which azophenylamine (semibenzidine) nitrazophenylamine and azonaphthylamine (seminaphtalidine) are the most conspicuous terms, is less clear than the constitution of the ureas, and of the phenyl-derivatives. These bases probably contain diatomic radicals which, in the series of aromatic alcohols, correspond to the hydrocarbons ethylene, propylene, etc., of the ordinary alcohols; these radicals are still somewhat uncertain.

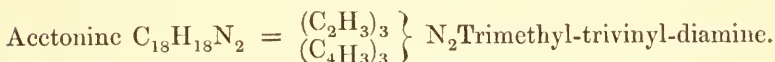


The constitution of these bodies requires to be elucidated by further researches. It deserves to be noticed, that of the two bases, azophenylamine and azonaphthylamine, which are generated by perfectly analogous reactions, the former is monacid, whilst the latter is diacid.

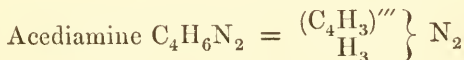
Scarcely better established are the views entertained regarding the constitution of the three well defined monacid diamines, amarine, acetone, and acediamine. In amarine, we may assume with great probability the existence of a diatomic radical $C_{14}H_6$ (stilbyl) :



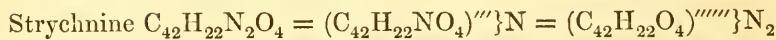
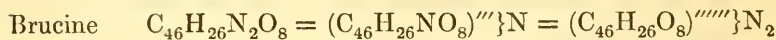
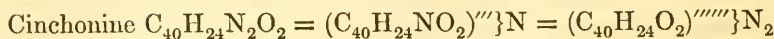
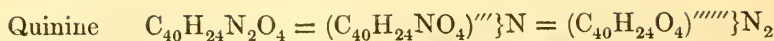
Acetone may possibly contain methyl and vinyl :



In acediamine, lastly, a triatomic molecule, homologous to the glycerin-radical, has been assumed :

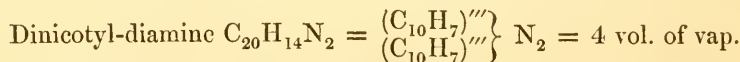


In almost absolute uncertainty remains, at this moment, the constitution of a numerous class of natural bases which contain 2 equivs. of nitrogen in their molecule, such as quinine, cinchonine, brucine, strychnine, etc. By a method, which will claim our attention bye-and-bye, Chemists have established that these substances no longer contain any unreplaced hydrogen ; but all attempts have, as yet, failed to eliminate and to characterise the replacing molecules. The bases in question are generally considered as diamines : but this view rests upon very slender foundation, and no subject connected with the history of the organic bases is more in need of further experiment. In the present state of our knowledge, we may translate the empirical formula of each of these bodies into monammonic and diammonic expressions.



The conception of these bodies as monamines involves the assumption of nitrogenous molecules among the substitution-materials, an assumption which appears justified by the frequent replacement—in artificial bases at least—of hydrogen by cyanogen, of which numerous illustrations have been already quoted. On the contrary, if we prefer to view them as diamines, we are obviously guided by the observation that some of these substances, like quinine and cinchonine, exhibit both a monatomic and a diatomic character in their combinations with acids,—uniting as they do with either one or two equivalents,—and that they are all decomposed by the action of heat, whilst well established monamines are generally volatile without decomposition. It deserves, however, to be noticed that artificial monamines in which the substitution is effected by nitrogenous molecules, are likewise apt to be altered under the influence of heat.

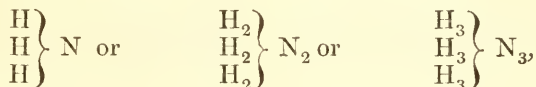
On the other hand, many Chemists are inclined to ascribe a diammonic character to nicotine, which, in one of the preceding sections, has been enumerated among the tertiary monamines. This substance is volatile without decomposition; expressed by the formula $\text{C}_{10}\text{H}_7\text{N} = (\text{C}_{10}\text{H}_7)''' \text{N}$, its molecule unites with 1 equiv. of acid. But the quantity expressed by this formula corresponds to 2 volumes of vapour, whilst ammonia, and all the volatile bases, the density of which has, as yet, been carefully examined, represent 4 volumes of vapour. On the assumption that the molecule of nicotine possesses a similar state of condensation, the formula of this substance has been doubled, when nicotine presents itself as a diamine, thus—



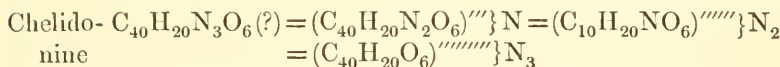
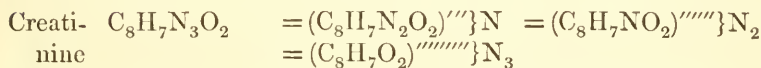
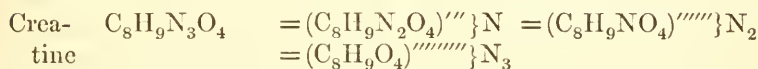
a formula which receives an additional support in the somewhat high boiling point (250°) of this compound.

c. Triamines.

Among the bases of animal or vegetal origin, there occur several which contain 3 equivs. of nitrogen; but, as their constitution is entirely unknown, we have no means to decide whether they are monamines, diamines, or triamines. Creatine, creatinine, and chelidonine, according as we derive them from either—



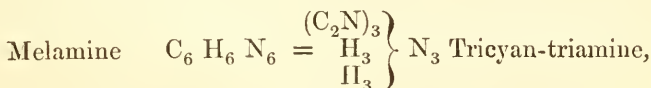
may be respectively represented by the following formulæ:—



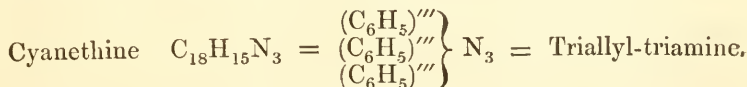
Since the existence of cyanogen-substitutes in nature is doubtful, they probably will be found to be triamines.

There are, in fact, only two artificial bases in which the triammonic character is somewhat distinctly pronounced.

These are: melamine which, when considered from this point of view, presents itself as tricyan-triamine:



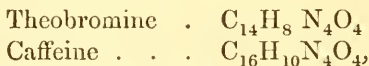
and cyanethine, the constitution of which is still doubtful, but in which we have probably to assume the triatomic allyl-radical of the glycerin-series:



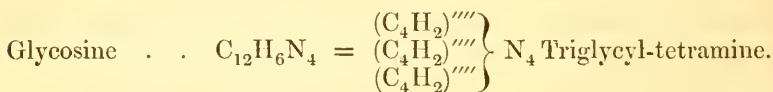
The accumulation of ammonia-molecules by no means appears

to have reached its climax in the formation of triamines. Under favourable circumstances, 4, 5, and perhaps even a larger number of equivalents of ammonia appear to be capable of coalescing into complex molecules of a higher order. We are thus led to the conception of d. *Tetramines* and e. *Pentamines*.

Among the natural bases several are found, which, like theobromine and caffeine—



contain 4 equivalents of nitrogen. The constitution of these bodies is unknown, but upon further investigation they may turn out to be tetramines. The only well characterised tetramine has been but lately discovered in the reaction of ammonia upon glyoxal. This tetramine, which appears to be diacid, and has been described as glycosine,—a name, by the way, which is apt to be confounded with the term glycocine, frequently used for glycocoll—probably contains a radical C_4H_2 (glycyl) of tetratomic substitution-power.



Pentamines appear to be produced by the action of certain metallic oxides upon ammonia. Recent researches have brought to light a numerous class of remarkable substances known by the name of cobalt-bases, in several of which a pentammonic character has been recognized. The history of these compounds, however, is still exceedingly imperfect.

The substances hitherto considered, however varied their constitution, are all true ammonias; in all of them the structure of the original molecule may still be more or less distinctly traced. We have now to examine a large class of bodies, which, although inseparably connected with the ammonias, nevertheless exhibit a different molecular construction.

When uniting with bodies of a different type, the molecule of ammonia gives rise to the formation of compounds in which the type of ammonia disappears. In its combinations with bodies of the water-type, or of the salt-type, we have no difficulty in perceiving

all the features of these very types. Combined with hydrochloric acid, ammonia no longer exhibits its peculiar odour, its powerful alkalinity, its volatility; the compound thus produced presents all the characters of a truly saline body; it shows, both in its physical and chemical properties, so unmistakeable an analogy with the chlorides of sodium and potassium, that Chemists have assumed in this compound the existence of a peculiar metal, the hypothetical *ammonium*. Similar, though less marked, is the change in the characters of ammonia when combined with bodies of the water-type. It is true that the solution of ammonia in water retains the characteristic features of ammonia-gas; the powerful odour, the volatility of this substance are scarcely diminished. Nevertheless, the chemical deportment of the solution presents so numerous and striking analogies with the solutions of the hydrates of potassa and soda,—bodies which undoubtedly are framed upon the water-type,—that the assumption of a similar construction of these several bodies is almost irresistible. It was in the conception of this similarity of construction, that the sagacity of Berzelius was led to view the solution of ammonia in water as a solution of hydrated oxide of ammonium, similar to the hydrated oxides of potassium and sodium which constitute our potassa- and soda-solutions.

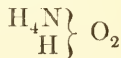
Hydrated oxide of
potassium.



Hydrated oxide of
sodium.

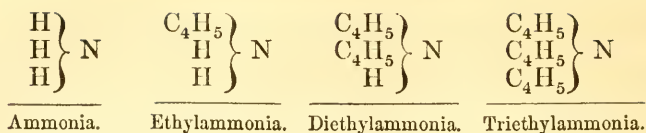


Hydrated oxide of
ammonium.

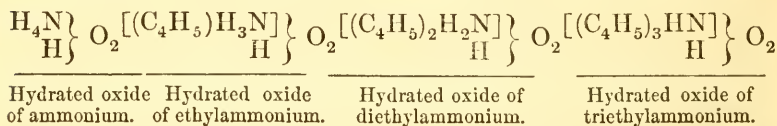


The progress of science has elicited a number of most remarkable confirmations of this view. United with the hydrated protoxide of platinum, ammonia furnishes a soluble alkali in which even the odour and volatility of ammonia have disappeared,—an alkali which, in most of its reactions, is apt to be confounded with the oxides of the alkali-metals. A host of similar bodies is formed when the basic derivatives of ammonia, and more especially those which we have enumerated as tertiary monamines, unite with bodies of the water-type.

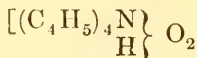
In the preceding section, ethylamine, diethylamine, and triethylamine, have been quoted as representatives of the primary, secondary and tertiary monamines; they are derived from ammonia by the successive replacement of 1, 2, and 3 equivs. of hydrogen by the corresponding number of ethyl-molecules.



The solutions of these bodies in water we regard, in accordance with the view taken of the solution of ammonia itself in water, as the hydrated oxides of ethyl- diethyl- and triethyl-ammonium.



All these solutions exhibit the general features of the ammonia-solution; neither the odour nor the volatility of the ethylamines is appreciably affected by the presence of the water. Doubts may, therefore, be entertained, and have been entertained, as to the propriety of assuming in these solutions bodies of a really different type. These doubts are, however, no longer admissible in the case of a remarkable class of compounds, generated by the replacement of the last equivalent of ammonium-hydrogen in the hydrated oxide of triethylammonium, its homologues and analogues. The compound,



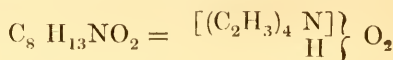
which has been designated as hydrated oxide of tetrethylammonium, altogether differs from the oxides of ammonium, ethyl-, diethyl- and triethyl-ammonium; odour and volatility have entirely disappeared, and we find triethylamine converted into a powerfully alkaline body, uniting in a very remarkable manner all the essential characters of the mineral alkalies. In hydrated oxide of tetrethylammonium and its homologues and analogues, we have a most undoubted representative of the water-type.

In the following table, we have united some of the most remarkable members of this group, the formation of which will claim our attention hereafter :

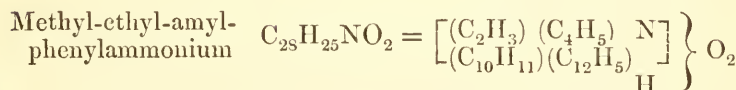
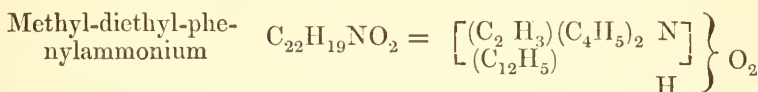
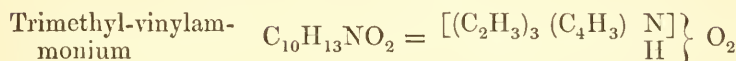
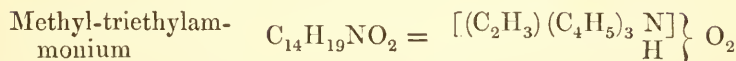
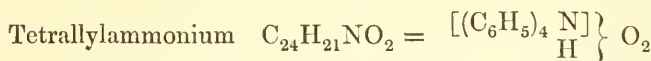
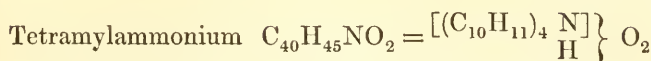
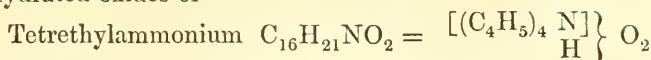
Basic Derivatives of ammonia constructed upon the water-type.

Hydrated oxide of—

Tetramethylammonium



Hydrated oxides of—

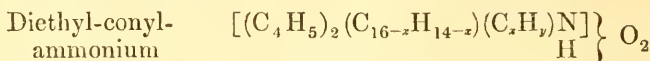
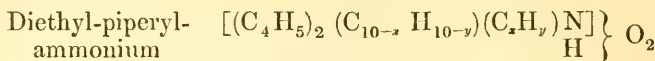


The members of this group may be conceived to arise out of the ammonias by the simple accession of the elements of alcohols. We are, therefore, not surprised to meet with a considerable number of bodies, the position of which in the system is not doubtful, although their constitution may not yet be sufficiently investigated. Any uncertainty which obtains with reference to the constitution of a secondary or tertiary monamine cannot possibly disappear by its transition into compounds corresponding to the water-type.

As we have seen, the constitution of piperylamine and conylamine is not finally established; but we have recognised these substances as undoubted secondary monamines. By the substitution of ethyl for their unreplaced hydrogen, these two bases are respectively converted into the well-defined tertiary monamines, ethyl-piperylamine and ethyl-conylamine; and by the accession, lastly, of the elements of ethylic alcohol, we arrive at two unequivocal representatives of hydrated oxide of ammonium. The uncertainty, however, regarding the constitution of piperylamine and conylamine, remains in the derivatives of these bases, and if, in representing the constitution of these derivatives, we want to exclude

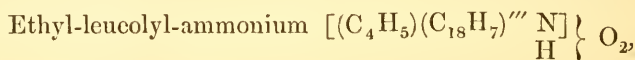
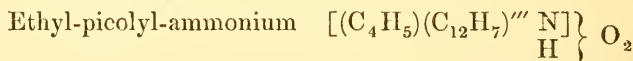
all hypothesis, we have to introduce into their formulæ the expressions originally elected for the secondary diamines:

Hydrated oxides of—



The constitution of the tar-bases picoline and leucoline is even less certain than that of piperidine and conine. All we know is that they must be viewed as tertiary monamines. They are likewise convertible into compounds constructed upon the water-type, which may be represented by the formulæ:

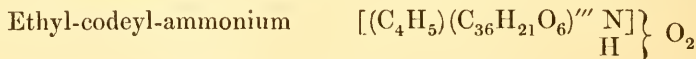
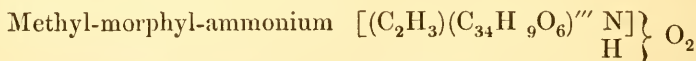
Hydrated oxides of—



in which the terms $(\text{C}_{12}\text{H}_7)'''$ and $(\text{C}_{18}\text{H}_7)'''$ simply express quantities of carbon and hydrogen, equivalent to H_3 , the molecular arrangement of which remains to be investigated.

The same remarks apply to those ammonium-derivatives, which are produced from natural tertiary monamines, such as morphine and codeine, by the addition of the elements of alcohols.

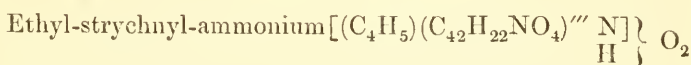
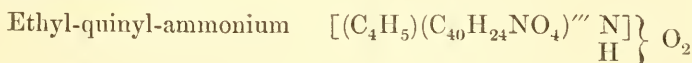
Hydrated oxides of—



In formulating the representatives of this group, which are derived from quinine, cinchonine, brucine, strychnine, etc., we meet with the same difficulty which presented itself in the consideration of the alkaloids themselves. We know that these bases contain no replaceable hydrogen; but, utterly unacquainted as we are with their constitution, we have at present no means of ascertain-

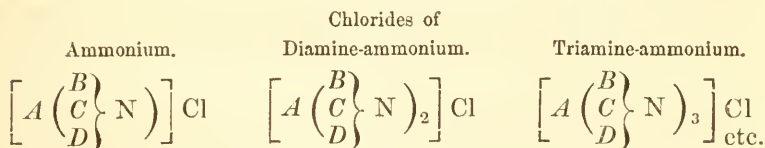
ing whether they are monamines or diamines. When they are regarded as monamines, the formulæ of their ethylic derivatives become similar to those of the preceding compounds; the formulæ of the quinine- and strychnine-compounds, for instance, assume in this case the following shape :

Hydrated oxides of—

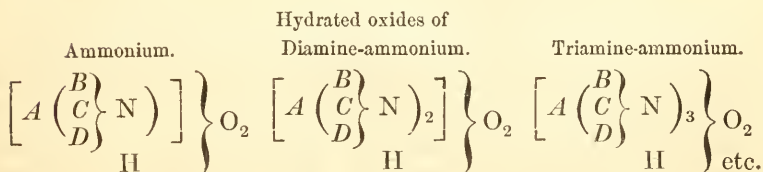


But we have seen that quinine and strychnine may be regarded with equal, and perhaps even with greater probability as diamines. Adopting this latter view, and endeavouring to adjust the formulæ of their derivatives to the water-type, we are led to the assumption that compound monatomic metals, similar to ammonium, may be formed by the association of 1 equiv. of hydrogen, not only with 1 molecule of ammonia, but with 2, and perhaps even with 3 molecules of ammonia; we arrive in this manner at compounds of monamine-ammonium (ammonium *par excellence*), diamine-ammonium, triamine-ammonium, etc., which in general terms may be thus expressed :

Derivatives constructed upon the chloride-of-sodium-type.



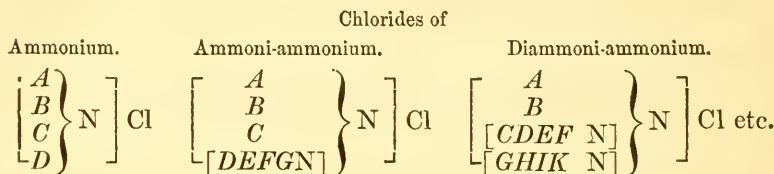
Derivatives constructed upon the water-type.



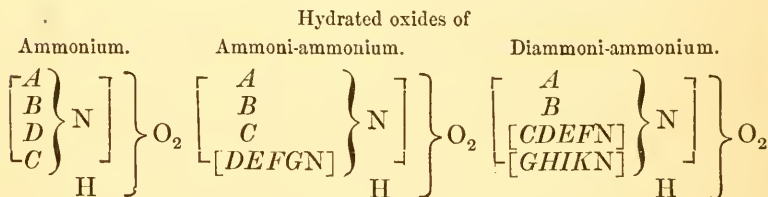
In other words, we have to assume the possibility of replacing

the hydrogen in ammonium by ammonium itself, or by its derivatives, an idea which may be illustrated by the following formulæ :

Derivatives constructed upon the chloride-of-sodium-type.

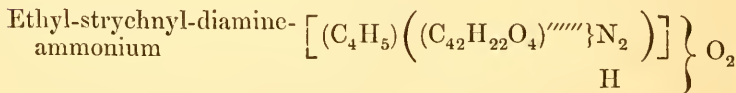
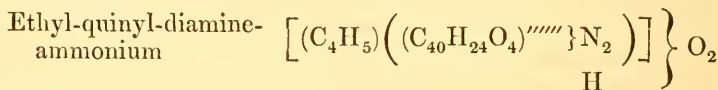


Derivatives constructed upon the water-type.

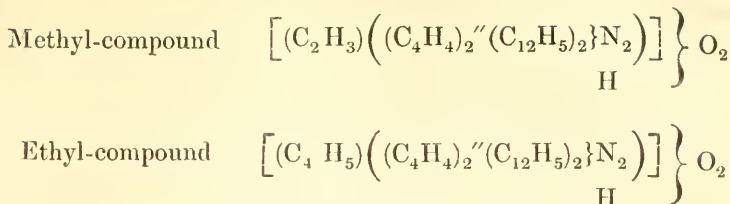


Very few of the compounds suggested by these formulæ have as yet been realized. The ethyl-derivatives of quinine and strychnine, which have led us to these considerations, must be viewed as diamine-ammonium-compounds, and may thus be formulated :

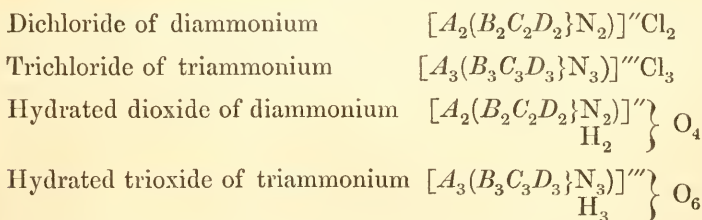
Hydrated oxide of—



There are very few other representatives of this class, and we may limit ourselves to quoting, as additional illustrations, the methyl- and ethyl-derivatives of an artificial diamine, the constitution of which is much better known than that of quinine and strychnine. Among the diammonic derivatives of phenylamine, a substance has been mentioned as diethylene-diphenyl-diamine; this body, which is diacid, absorbs the elements of methylic or ethylic alcohol, and is thus converted into compounds of the formulæ :



All the ammonium-derivatives of monamines or diamines, hitherto considered, correspond to one molecule of water; they are,—if such a term be permitted,—monhydric. But we know,—and the recent elaboration of the theory of polyatomic alcohols has particularly assisted in establishing this point,—that the entrance of polyatomic radicals into a system is capable of linking together 2, 3, and perhaps even more, molecules of water, exactly as we have seen that 2, 3, or more molecules of ammonia may associate together. We thus arrive at a series of water-derivatives, which may be designated as dihydric, trihydric, and, in general, as polyhydric. Again, among the substances constructed upon the type of chloride of sodium, we meet with many instances of a similar accumulative tendency. Hydrated oxide of ammonium and its homologues being monhydric derivatives of water, and chloride of ammonium corresponding to one molecule of salt, it is but consistent to anticipate the existence of di- and trihydric ammonium-compounds, and of ammonium-salts corresponding to 2 or 3 molecules of chloride of sodium. We are thus led to the conception of diammonium- and triammonium-compounds, which may thus be formulated:

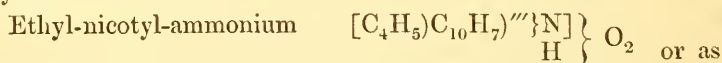


In conceiving the existence of such compounds, it must be admitted that, in this case, theory is somewhat in advance of experiment. As yet but few terms of this group have been ob-

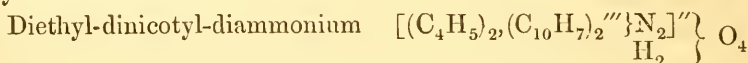
tained; but very few also have been the efforts made to produce them.

In one of the preceding sections, we have stated that the opinions of Chemists regarding the formula of nicotine remain divided,—that some consider this base as a tertiary monamine, whilst others prefer to classify it with the tertiary diamines. Nicotine, like the rest of the tertiary amines, assimilates the elements of alcohols, and, according as we adopt, for this base, either the monatomic or the diatomic formula, we have to represent the ethyl-derivatives of nicotine as:

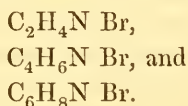
Hydrated oxide of—



Hydrated dioxide of—

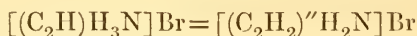


It is very probable that Chemists will ultimately recognize as diammonium-compounds a series of substances which are formed by the substitution of olefiant gas and its homologues for the hydrogen in ammonia. Under the influence of dibromide of ethylene, ammonia is converted into a mixture of several salts, to which analysis has assigned the following composition:



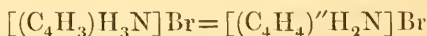
The constitution of these compounds has received different interpretations: some Chemists are inclined to assume in these substances the existence of monatomic radicals C_2H , $-\text{C}_4\text{H}_3$, $-\text{C}_6\text{H}_5$, whilst others believe them to contain the diatomic radicals C_2H_2 , $-\text{C}_4\text{H}_4$, $-\text{C}_6\text{H}_6$. These views are embodied in the following names and formulæ:

Bromide of
formyl-
ammonium



Bromide of
methylene-
ammonium.

Bromide of
vinyl-
ammonium



Bromide of
ethylene-
ammonium.

Bromide of allyl- ammonium	$[(C_6H_5)H_3N]Br = [(C_6H_6)''H_2N]Br$	Bromide of propylene- ammonium.
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A third view, based upon the general chemical character of these bodies, and especially upon their mode of formation, claims them as diammonium-compounds, containing 1, 2, or 3 molecules of the diatomic ethylene in the place of 2, 4, or 6 equivalents of hydrogen, when the formulæ originally assigned to them undergo a slight correction, and assume the following shape :

Dibromide of ethylene-diammonium $[(C_4H_4)''H_6N_2]''Br_2$

Dibromide of diethylene-diammonium $[(C_4H_4)_2''H_4N_2]''Br_2$

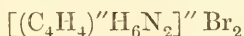
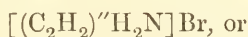
Dibromide of triethylene-diammonium $[(C_4H_4)_3''H_2N_2]''Br_2$

It is obvious that the discovery of

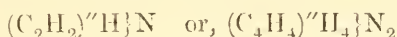
Dibromide of tetrethylene-diammonium $[(C_4H_4)_4''N_2]''Br_2$

is required to complete this list, when the series of diatomic ammonium-compounds will become perfectly analogous to the series of monatomic bodies, produced by the substitution of methyl, ethyl, etc., for the hydrogen in ammonium.

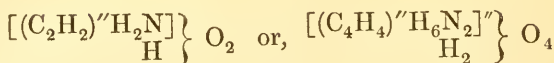
Further researches are necessary in order to decide which of these views will ultimately be received as truly representing the constitution of these remarkable bodies. It may even now be stated that these substances exhibit in many directions a deportment perfectly different from what analogy could have suggested ; for whilst the monatomic ammonium-salts cannot be decomposed without producing bodies belonging to another type, yielding as they do either a hydrated oxide of ammonium (water-type) or water and a monamine (ammonia-type), it would appear that from the salts which have just engaged our attention, the bases may be liberated *without* change of type. The deportment of chloride of ethylammonium would lead us to expect that the first term of our series, whether viewed as—



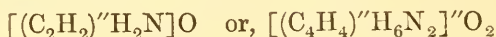
would yield under the influence of oxides, either a monamine or diamine—



or, possibly, the hydrated oxide of an ammonium or of a diammonium:



Instead of this, we produce in reality a volatile oxygenated compound, containing either



in which the salt-type is obviously preserved.

In the preceding remarks we have given an outline of the views at present entertained regarding the constitution of the organic bases; we have now briefly to examine the circumstances under which these substances are generated.

Formation of Organic Bases.

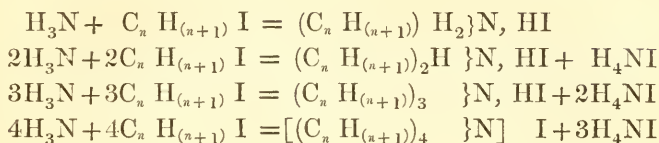
Nothing certain is known regarding the genesis of natural bases. It is obvious that these bodies originate from ammonia, which is known to be the source of nitrogen in all nitrogenous vegetal principles. But as yet we are unacquainted with the compounds, under the influence of which the transformation of ammonia into vegetal alcaloids takes place. The following statements, therefore, refer exclusively to artificial bases.

A very considerable number, indeed the majority of these substances are formed by

Direct substitution of Organic Radicals for the Hydrogen in Ammonia.

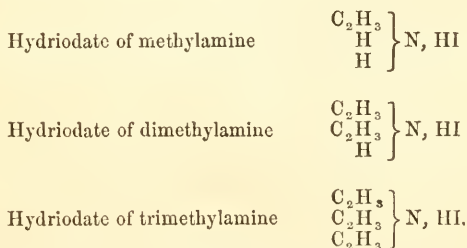
This substitution has been hitherto chiefly effected by the action of the bromides and iodides of the common alcohol-radicals. According as 1, 2, 3, or 4 molecules of ammonia are acted upon by 1, 2, 3, or 4 equivalents of the alcohol-iodide, we obtain in this case the hydriodate of a primary, secondary, or tertiary monamine, homologous to ammonia, or lastly, the iodide of a substituted ammonium.

The following equations, in which n represents an even number, illustrate these reactions :



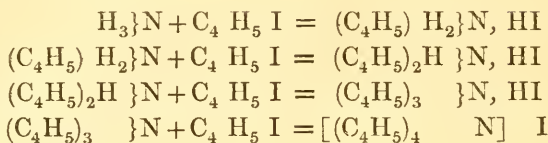
These different compounds are almost always produced simultaneously, but by no means in equal quantities. On submitting ammonia to the action of iodide of methyl, the five iodides, iodide of ammonium, of methyl-, dimethyl-, trimethyl-, and lastly of tetramethyl-ammonium are formed together, but the last, and consequently also the first, term of the series are obtained in very considerable excess.* In the reaction between ammonia and iodide of ethyl, on the other hand, the substitution occurs more gradually, so that we meet with less difficulty in isolating the several terms of the series. The action of iodide of ethyl upon ammonia invariably produces a quantity of hydriodate of ethylamine, although some of the higher products, and especially diethylamine, are always formed in very appreciable proportions. Ethylamine, separated from the hydriodate by means of potassa, and again treated with iodide of ethyl, yields chiefly the hydriodate of diethylamine; the base separated from the latter gives, with iodide of ethyl, hydriodate of triethylamine. Triethyl-

* Both the nomenclature and the formulæ at present in use for the salts of the organic bases, are far from consistent. The salts produced by the action of hydriodic acid upon methylamine, dimethylamine, and trimethylamine, are generally designated as



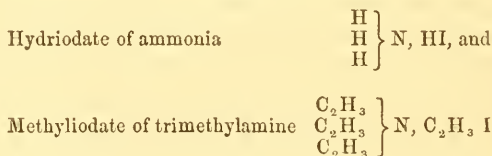
On the other hand, we speak almost always of iodide of ammonium, and invariably

amine lastly unites directly with iodide of ethyl, to form iodide of tetrethylammonium.

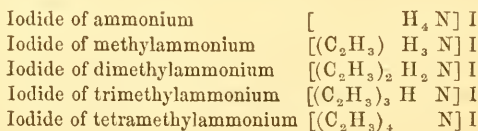


Provided we spare neither time nor alcohol-iodide, the last iodine-compound of the series is almost always readily obtained in a state of perfect purity. The tetrammonium-compound once procured, there is no longer any difficulty in preparing the triamine. By treatment with oxide of silver, the iodide is converted into the hydrated oxide of the tetrammonium, and the distillation of the latter furnishes the triamine: alcohols, or the elements of alcohols, being eliminated. Thus, hydrated oxide of tetramethylammonium splits into trimethylamine and methylic alcohol, whilst the corresponding

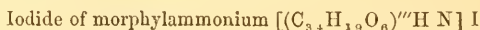
of iodide of tetramethylammonium. In accordance with the above names and formulæ, these two salts should be represented as



Or we should view them all as ammonium-compounds, and express them by the following formulæ—

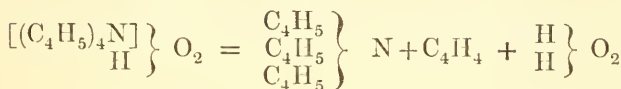
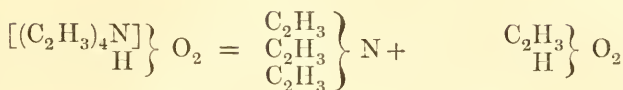


To be consistent, however, it would then also become necessary to adopt for hydriodate of morphine the expression—



In order to avoid too serious a conflict with the common chemical language, the salts of monamines and diamines, etc., have been generally represented as compounds of ammonia with hydrogen-acids.

term of the ethyl-series furnishes, together with triethylamine, water and olefiant gas:



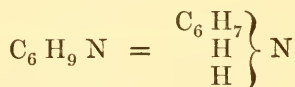
If we consider the number of alcohols already known, which is sure to be greatly augmented by the further development of organic chemistry,—if we recollect, moreover, that the several equivalents of hydrogen in ammonia and in ammonium are by no means always replaced by the same radicals, we conceive the extraordinary multitude and variety of basic compounds which the endless permutations of this method permit us to obtain.

The successive replacement of the hydrogen in ammonia by means of the alcohol-iodides, whilst enabling us to produce an almost unlimited number of new compounds, furnishes us at the same time with a most valuable method—in fact, almost the only method which is at present at our disposal—of studying the constitution of organic bases, whether natural or artificial. Supposing that the composition of an organic base has been carefully ascertained by elementary analysis, that its equivalent has been successfully determined by the examination of its salts, especially the double salts with dichloride of platinum or trichloride of gold, supposing, in fact, the formula of the substance well established, we are still in utter ignorance regarding its molecular construction. By treating the body under examination with iodide of methyl or ethyl, by ascertaining the number of methyl- or ethyl-equivalents which it is capable of fixing, we establish the degree of substitution of the base, we determine whether it is a primary, a secondary, a tertiary monamine, or lastly a compound corresponding to hydrated oxide of ammonium. A primary monamine thus treated will be found to fix 3 equivs. of methyl, a secondary 2 equivs., a tertiary monamine 1 equiv. of methyl: a base corresponding to hydrated oxide of ammonium is no longer changed under the influence of these agents.

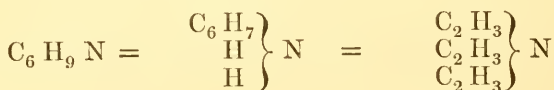
This method has already supplied some important information

regarding the molecular construction of a variety of bases: indeed the classification which we have attempted in the preceding sections is almost exclusively based, as must be now obvious, upon the deportment of the bases with the alcohol-iodides.

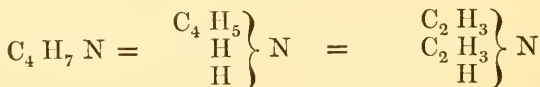
Among the ammonia-derivatives which exist in the brine of salt herrings, there is one the analysis of which has led to the formula $C_6 H_9 N$. The Chemist who first observed this substance, very naturally considered it as the primary monamine corresponding to propylic alcohol, as propylamine:



On treatment, however, with iodide of methyl, it was observed that this base is not capable of absorbing more than 1 equiv. of methyl, being at once converted into a compound corresponding to hydrated oxide of ammonium. This deportment unequivocally characterised it as a tertiary monamine, which was forthwith recognised as trimethylamine.



By the action of soda-lime upon the compound of aldehyde with bisulphite of ammonium, a volatile base is formed which, for a long time, was believed to be ethylamine. By a perfectly analogous mode of proceeding it was found to be dimethylamine;



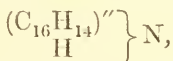
The deportment with iodide of ethyl characterises phenylamine and its homologues as primary, leucoline and its homologues as tertiary, monamines. In a similar manner the bases of the pyridine-series, and thialdine, together with its homologues, have been recognised as tertiary monamines.

Applied also to natural bases, this method has been fertile in results. Conine has been established as a secondary, codeine

and morphine as tertiary, monamines. Nicotine is, as we have seen, either a tertiary monamine or a tertiary diamine, and the same remark applies to quinine, cinchonine, quinidine, brucine, and strychnine.

The action of the iodides or bromides of the alcohol-radicals upon bases, whilst fixing in a most satisfactory manner their degree of substitution, unfortunately fails altogether to reveal the nature of the replacing molecules.

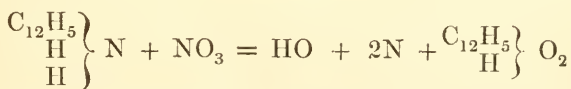
The analysis and the determination of the equivalent of conine, had led to the formula $C_{16}H_{15}N$. By treatment with iodide of ethyl, it had been ascertained that this base fixes 2 equivs. of ethyl, being thereby converted into a compound corresponding to hydrated oxide of ammonium. This experiment was sufficient to characterize conine as a secondary monamine,



but it gave us no clue to the nature of the radicals which are substituted for the 2 equivs. of hydrogen; these 2 equivs. of hydrogen may be replaced by a diatomic molecule $C_{16}H_{14}$, or, by two monatomic molecules C_8H_7 , or generally by two monatomic molecules $C_{16-x}H_{14-y}$ and C_xH_y .

Many experiments have been made with the view of eliminating the radicals in a recognizable form from the bases. These experiments have as yet been but partially successful. We have already seen that the distillation of an ammonium-base yields the corresponding triamine with separation of an alcohol or of its products of decomposition. Less fortunate has been the attempt at separating the radicals from the monamines. The sole reaction, which deserves to be noticed, arises from the treatment of the bases with nitrous acid, when the nitrogen of both compounds is eliminated as gas, the radical separating in the form of an oxide.

Under the influence of nitrous acid, phenylamine yields phenyl-alcohol and nitrogen.

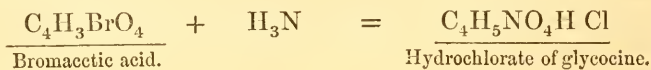


The reaction, however, by no means furnishes the amount of phenyl-alcohol indicated by theory; a large quantity of this substance is, by the continued action of nitrous acid, converted

into nitrophenyl-alcohol and resinous products. In a similar manner, tolylamine yields almost exclusively nitrocresyl-alcohol. Ethylamine and amylamine are converted into the nitrites of ethyl and of amyl. In all these reactions, other products are simultaneously generated. Recent experiments have proved that this process requires a further study. It has been observed that several phases must be distinguished: in the first phase, the base, assimilating the elements of water, appears simply to be split into alcohol and ammonia; the latter then, under the influence of nitrous acid, yields nitrogen and water. Thus, phenylamine, in the first stage of the process, furnishes an appreciable quantity of ammonia; ethylphenylamine similarly treated, gives rise, in the commencement of the reaction, to the formation of ethylamine.

To find a simple method for the elimination of the radicals from the organic bases, is the task of our time. The discovery of such a method, whilst enabling the Chemist to decompose the most complicated alkaloids into their components, cannot fail ultimately to lead to the artificial production of these alkaloids themselves.

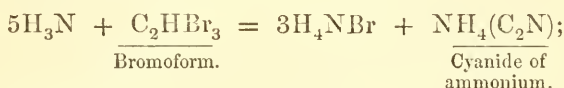
In using the method of introducing electropositive radicals into ammonia, by means of their bromides and iodides, the radicals of the ordinary monatomic alcohols, corresponding to the series of fatty acids, have been almost exclusively employed as materials of substitution. The action of the chlorides and bromides of the oxygenated radicals upon ammonia, produces the numerous class of neutral bodies, which we shall hereafter consider under the head of amides. The only instance of the formation of a weak base in a reaction of this kind, has been recently observed, namely, the transformation of chloracetic and bromacetic acid into glycocine (glycocoll).



The application, to the bromides and iodides of the diatomic and triatomic alcohols, of a method, which has been so fertile in the case of the monatomic alcohols, promises a rich harvest of results. Even now some very remarkable products have been obtained by the action of ammonia on the dichloride and dibromide of ethylenc. We have already alluded to these substances

which by some are considered monammonic, by others, diammonic bases. Their study is attended with unusual difficulties, and as yet their true nature is scarcely made out.

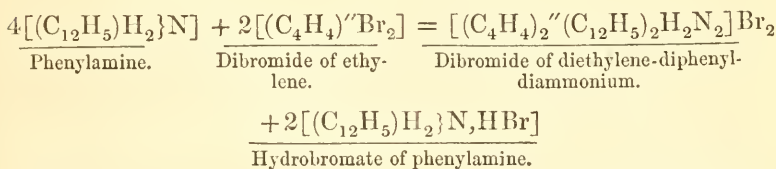
The deportment of ammonia with the bromides and iodides of the triatomic alcohols, has been scarcely studied. The only cases examined are the action of tribromide of formyl (bromoform), and that of tribromide of allyl upon ammonia; the product of the former is cyanide of ammonium—



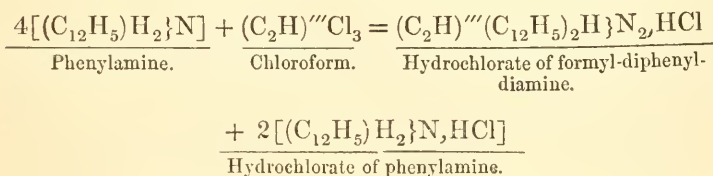
in the latter reaction, the bromide of a compound ammonium is produced, in which 2 equivs. of hydrogen are replaced by 2 equivs. of a monatomic brominetted hydrocarbon ($\text{C}_6\text{H}_4\text{Br}$).



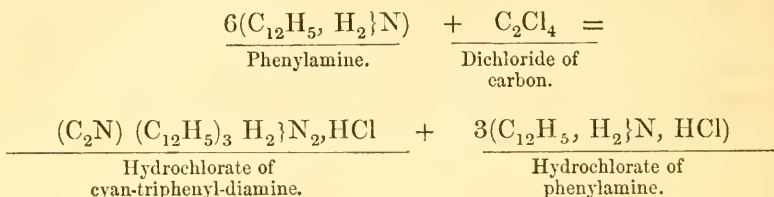
Some further progress has been made in the study of the action which the compounds of the diatomic alcohols exercise upon the monamines, especially upon phenylamine. In most of these cases, diammonic and even triammonic bases are produced. Phenylamine and dibromide of ethylene, furnish the dibromide of diethylene-diphenyl-diammonium.



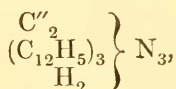
Phenylamine and chloroform, give together with hydrochlorate of phenylamine, the hydrochlorate of formyl-diphenyl-diamine.



Phenylamine is acted upon even by the so-called bichloride of carbon C_2Cl_4 , a monacid base being produced, which we have mentioned as cyan-triphenyl-diamine.



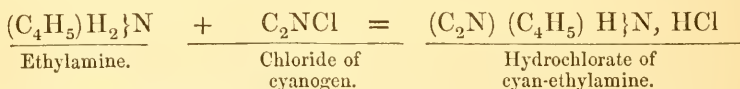
It deserves, however, to be noticed, that the substance in question may also be viewed as a triamine, as



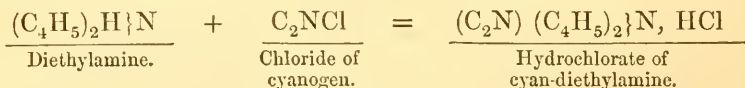
for it is by no means experimentally proved that the carbon, derived from the chloride, assumes, in the new base, the form of cyanogen.

The action of chloride and bromide of cyanogen on ammonia and its derivatives deserves, lastly, to be mentioned. According to the nature of the base submitted to these agents, the new compound produced is either a monamine, a diamine, or even a triamine.

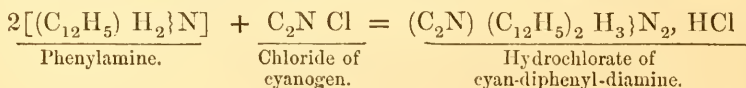
Ethylamine furnishes, with chloride of cyanogen, a secondary monamine.



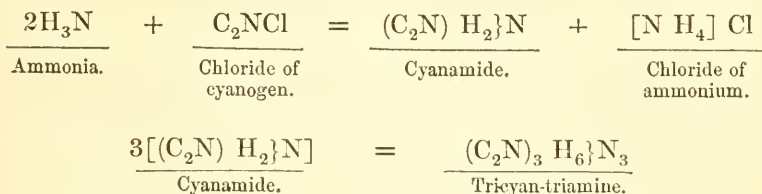
The same reaction converts diethylamine into a tertiary monamine.



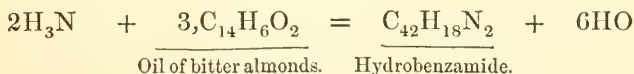
Phenylamine, on the other hand, yields, with chloride of cyanogen, melaniline, a well characterised monacid diamine.



Finally, the action of chloride of cyanogen upon ammonia, gives rise to the formation of the neutral cyanamide, which, under the influence of heat, is transformed by molecular rearrangement into melamine, a well defined monacid triamine.

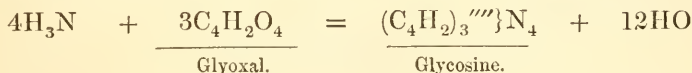


In the processes hitherto examined, the hydrogen of ammonia is eliminated by the action of iodides, bromides, and chlorides. This elimination may also be effected by oxygen-compounds; but the number of bases, thus obtained, is comparatively small. The agents capable of producing this effect are chiefly the aldehydes. As illustrations we may quote the formation of amarine (tristilbyl-diamine) by the action of oil of bitter almonds upon ammonia, that of furfurine from furfurol, and lastly, the formation of the remarkable tetramine, glycosine. In most of these cases neutral compounds, the so-called hydramides, are first produced, in which basic properties are developed by boiling with potassa, or by exposure to a temperature of 140°—160°C. Oil of bitter almonds yields, with ammonia, hydrobenzamide;

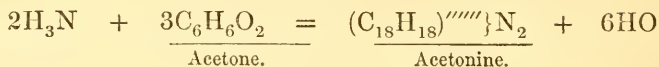


Hydrobenzamide is subsequently converted, by a simple molecular transposition, into amarine.

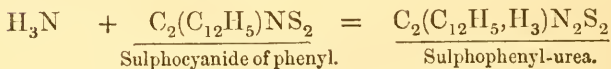
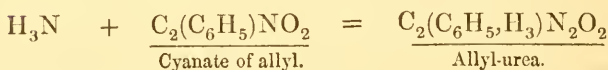
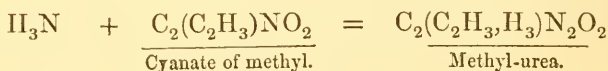
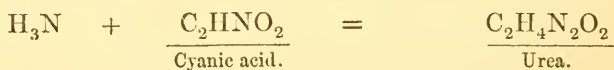
Ammonia and glyoxal yield directly glycosine:



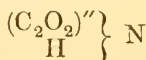
It appears that the acetones lend themselves to a similar reaction. As yet, only the acetone, *par excellence*, has been submitted to this process.



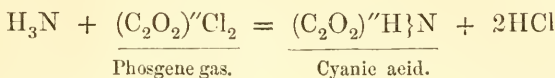
In the production of bases by the action of iodides, bromides, chlorides, and oxides, the hydrogen of the ammonia separates in the form of hydriodic, hydrobromic, or hydrochloric acid, or in the form of water. We are, however, acquainted also with a great number of cases, in which the formation of organic bases is effected by the direct union of ammonia with a variety of organic compounds, *without* the elimination of a second compound. Direct combination of this kind is chiefly observed in the formation of the numerous class of bases known as *ureas*, which are chiefly formed by the association of ammonia and cyanic acid, and of their derivatives.



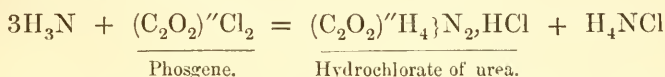
At the first glance, it would appear that processes of this kind exclude the conditions of substitution, since the ureas are the sole products of the reaction. But the apparent anomaly disappears if we recollect that the ureas are diamines, and that one of the ammonia-constituents, cyanic acid, is a product of substitution of ammonia, so that we may consider this substance as a secondary diamide, as



In fact, according to recent researches, cyanic acid is formed by a process of substitution in the action of dichloride of carbonyl $(C_2O_2)''Cl_2$ (phosgene gas) upon ammonia :

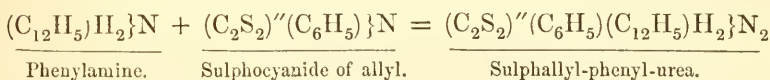
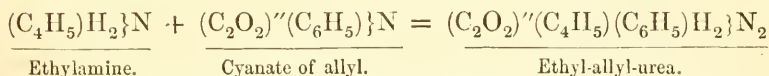
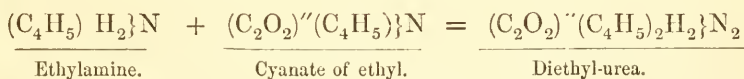


which, in the moment of its formation, combines with the excess of ammonia, forming urea :

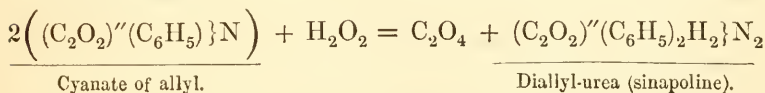
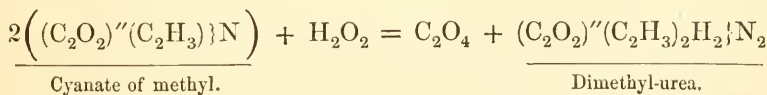


It is obvious that this interesting formation of urea involves a true process of substitution, and that it is very much in favour of the view we have taken of the constitution of this class of compounds.

The same remarks apply to the formation of the ureas of higher degrees of substitution, which are formed by the action of the cyanates on monamines :



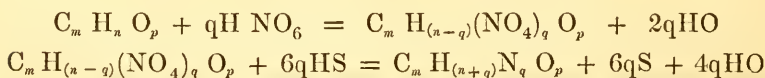
The same compounds are also obtained by the action of water upon the cyanic ethers, when one equivalent of ether is decomposed with formation of carbonic acid and of a monamine, which joins the second equivalent.



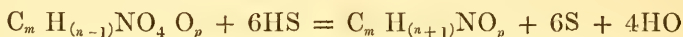
Formation of Organic Bases by the Reduction of Nitro-compounds.

A great number of organic bodies, as is well known, when submitted to the action of nitric acid, lose part of their hydrogen, for which the elements of hyponitric acid are substituted. The nitro-compounds thus produced suffer under the influence of reducing agents, and more particularly of sulphuretted hydrogen,* a remarkable transformation, which consists in the substitution of NH_2 for NO_4 , or of H_2 for O_4 .

These successive changes are represented by the following equations:



In the majority of cases $q=1$; that is, only 1 eq. of hydrogen is replaced, when the latter equation assumes the following shape:

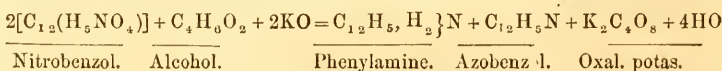


The nature of the compound $\text{C}_m \text{H}_{(n+1)}\text{NO}_p$, is essentially determined by the chemical character of the body $\text{C}_m \text{H}_n \text{O}_p$. From observation it would appear that the products are bases, when the mother-compounds are neutral bodies; that they are, on the other hand, acids, or substances capable of acting both like acids and bases, when the mother-compounds possess the character of acids.

* The original mode of proceeding was to treat the alcoholic solution of the nitro-compound with sulphuretted hydrogen, to digest the saturated solution, and to complete the action of the sulphuretted hydrogen by ebullition.

Hydrogen in *statu nascenti* (zinc and sulphuric acid) also transforms the nitro-compounds, though more slowly. Very conveniently a mixture of iron-filings and acetic acid may be employed; in many cases, such as the preparation of phenylamine and naphthylamine, this process yields much better results than treatment with sulphide of ammonium. The reduction of nitro-compounds may be likewise effected by arsenite of potassium and by phosphorus in the presence of caustic alkalis.

In a few cases, the reduction has been effected by the action of organic substances upon nitro-compounds. Nitrobenzol, when treated with an alcoholic solution of potassa, furnishes, together with several other products, phenylamine and azobenzol. This process is not sufficiently elaborated, but one of its phases, involving the formation of azobenzol and phenylamine, appears to consist in the deoxidation of the nitro-compound by the alcohol, which is converted into oxalic acid:



When $p = 0$, that is, when the mother-compound is a hydrocarbon, the base produced is a primary monamine:

$\frac{C_{12}H_6}{\text{Benzol.}}$	$\frac{C_{12}(H_5, NO_4)}{\text{Nitrobenzol.}}$	$\frac{C_{12}H_5, H_2\}N}{\text{Phenylamine.}}$
$\frac{C_{14}H_8}{\text{Toluol.}}$	$\frac{C_{14}(H_7, NO_4)}{\text{Nitrotoluol.}}$	$\frac{C_{14}H_7, H_2\}N}{\text{Tolylamine.}}$
$\frac{C_{20}H_8}{\text{Naphthalin.}}$	$\frac{C_{20}(H_7, NO_4)}{\text{Nitronaphthalin.}}$	$\frac{C_{20}H_7, H_2\}N}{\text{Naphtylamine.}}$

In a similar manner, basic compounds—most of them of still doubtful constitution—have been obtained from the nitro-compounds of

a. *Oxygenated Compounds.*

$\frac{C_{14}H_8O_2}{\text{Anisol.}}$	$\frac{C_{14}(H_7, NO_4)O_2}{\text{Nitransisol.}}$	$\frac{C_{14}H_9NO_2}{\text{Anisidine.}}$
$\frac{C_{14}H_6O_4}{\text{Benzoic acid.}}$	$\frac{C_{14}(H_5, NO_4)O_4}{\text{Nitrobenzoic acid.}}$	$\frac{C_{14}H_7NO_4}{\text{Benzamic acid.}}$

b. *Nitrogenous compounds.*

$\frac{C_{12}H_5N}{\text{Azobenzol.}}$	$\frac{C_{12}(H_4, NO_4)N}{\text{Nitrazobenzol.}}$	$\frac{C_{12}H_6N_2}{\text{Diphenine.}}$
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c. *Compounds containing Oxygen and Nitrogen.*

$\frac{C_{14}H_7NO_2}{\text{Benzamide.}}$	$\frac{C_{14}(H_6, NO_4)NO_2}{\text{Nitrobenzamide.}}$	$\frac{C_{14}H_8N_2O_2}{\text{Carbanilamine.}}$
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d. *Compounds containing Oxygen and Sulphur.*

$\frac{C_{24}H_{10}S_2O_4}{\text{Sulphobenzide.}}$	$\frac{C_{24}(H_9, NO_4)S_2O_4}{\text{Nitrosulphobenzide.}}$	$\frac{C_{24}H_{11}NS_2O_4}{\text{Sulphobenzamine.}}$
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Dinitro-compounds, when submitted to reducing agents, are capable of undergoing two different changes. They very frequently exhibit the deportment of the mononitro-compounds, exchanging H_2 for O_4 , with formation of bases, in which one or several equivalents of hydrogen are replaced by hyponitric acid :

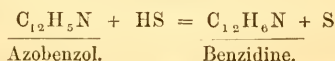
$\frac{C_{12}H_6}{\text{Benzol.}}$	$\frac{C_{12}[H_4(NO_4)_2]}{\text{Dinitrobenzol.}}$	$\frac{[C_{12}(H_4, NO_4)], H_2\}N}{\text{Nitrophenylamine.}}$
$\frac{C_{14}H_8O_2}{\text{Anisol.}}$	$\frac{C_{14}[H_5(NO_4)_3]O_2}{\text{Trinitranisol}}$	$\frac{C_{14}[(H_7(NO_4)_2)O_2\}N}{\text{Dinitranisidine.}}$

The second and third equivalents of hyponitric acid, behave, in these cases, like hydrogen.

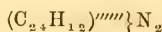
The reduction extends but rarely to a second equivalent of hyponitric acid. The basic compounds thus produced correspond to 2 equivs. of ammonia; they are diamines, the nature of which is, however, scarcely fixed by experiment.

$\frac{C_{20}H_8}{\text{Naphtalin.}}$	$\frac{C_{20}[H_6(NO_4)_2]}{\text{Dinitronaphtalin.}}$	$\frac{C_{20}H_{10}N_2}{\text{Azonaphtylamin.}}$
$\frac{C_{26}H_{10}O_2}{\text{Benzophenone.}}$	$\frac{C_{26}[H_8(NO_4)_2]O_2}{\text{Dinitrobenzophenone.}}$	$\frac{C_{26}H_{12}N_2O_2}{\text{Flavine (diphenyl-urca ?).}}$
$\frac{C_{14}H_6O_4}{\text{Benzoic acid.}}$	$\frac{C_{14}[H_4(NO_4)_2]O_4}{\text{Dinitrobenzoic acid.}}$	$\frac{C_{14}H_8N_2O_4}{\text{Benzodiamic acid.}}$
$\frac{C_{24}H_{10}S_2O_4}{\text{Sulphobenzide.}}$	$\frac{C_{24}[H_8(NO_4)_2]S_2O_4}{\text{Dinitrosulphobenzide.}}$	$\frac{C_{24}H_{12}N_2S_2O_4}{\text{Sulphobenzodiamine.*}}$

* The formation of benzidine should not be left unmentioned. It is obtained by the action of reducing agents, sulphuretted hydrogen or sulphurous acid, upon azo benzol :



We are utterly ignorant of the constitution of benzidine, but it can scarcely be doubted that this substance is a diacid diamine, and that its molecule is represented by the formula

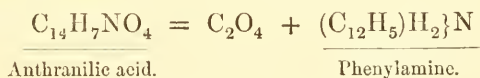


Formation of Organic Bases by the Decomposition of Nitrogenous Substances.

The bases generated in this manner are exceedingly numerous; they belong to very different groups of Organic Chemistry, and are produced by the greatest variety of agents.

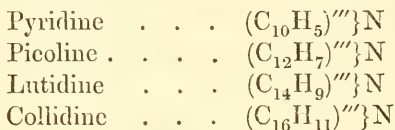
The destructive distillation of nitrogenous substances, has produced a rich harvest of organic bases. A great variety of metamorphoses may be accomplished, depending on the composition of the body distilled, and on the temperature to which it is exposed. In most cases, part of the carbon separates as carbonic acid, whilst the nitrogen is eliminated, partly as ammonia, partly associated with the rest of the carbon, and some hydrogen in the form of derivatives of ammonia. Generally water is an accessory product.

Anthranilic acid, submitted to distillation, splits into carbonic acid and phenylamine:



The dry distillation of indigo likewise yields phenylamine; the same base, together with a host of others, is generated by the destructive distillation of coal and animal matter.

Together with phenylamine, the products of distillation of coal, contain a series of homologous tertiary monamines, isomeric with the primary monamines of the phenyl-group:



In coal gas-naphtha are found, moreover, three tertiary monamines of another homologous series:



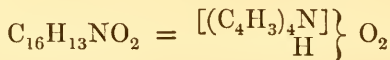
The series of pyridine-bases also exists in Dippel's Oil, associated with a great number of the ordinary alcohol-bases:

Methylamine . . .	(C ₂ H ₃)H ₂ }N
Ethylamine . . .	(C ₄ H ₅)H ₂ }N
Propylamine . . .	(C ₆ H ₇)H ₂ }N
Butylamine . . .	(C ₈ H ₉)H ₂ }N
Amlyamine . . .	(C ₁₀ H ₁₁)H ₂ }N

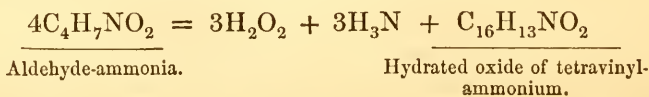
The series of pyridine-bases has also been found among the products of distillation of Devonshire shale, which contain, moreover, parvoline C₁₈H₁₃N, a higher term of the same series.

The processes by which bases are generated in the destructive distillation of vegetal and animal substances, are obviously extremely complicated, and can scarcely be traced in formulæ. The products of distillation of coal contain only a comparatively small proportion of organic bases, evidently because the nitrogenous principles from which they arose were present only in small quantity; and, moreover, because a portion of nitrogen is eliminated in the form of ammonia. We may assume that these bases owe their origin to the albuminous principles of the plants converted into coal. Starting on this supposition, Chemists have examined the products obtained by distilling those parts of plants, which are rich in nitrogen. All these products contain a variety of bases; but they are not yet sufficiently examined. Thus the distillation of beans has furnished a base, which appears to contain C₁₀H₆N (C₁₀H₇N?), and for which the name fabine has been proposed. Bases have also been found among the products of distillation of turf.

Among the bases generated by processes of destructive distillation, a remarkable product, obtained by the action of heat on aldehyde-ammonia, deserves to be mentioned. The formation of this substance, which appears to be hydrated oxide of tetravinyl-ammonium,



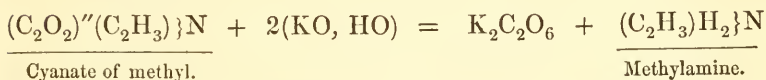
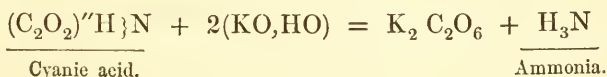
has not been sufficiently studied, but may probably be represented by the following equation :



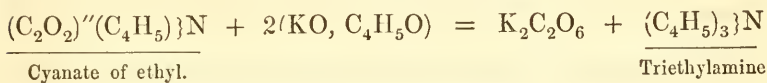
Results, similar to those produced by the destructive distillation of nitrogenous substances, are obtained by the action of the

hydrated alkalies, frequently by simply boiling them with a concentrated solution of potassa. The action of such powerful agents however, generally induces a more definite decomposition.

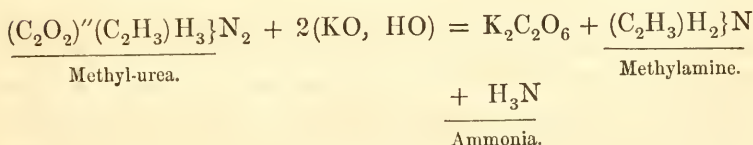
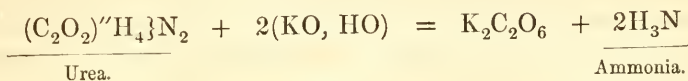
As the finest illustrations of this reaction, the transformations of the cyanic ethers and of the compound ureas must be quoted. Under the influence of an hydrated alkali, cyanic acid assimilates 2 equivs. of water, and splits into carbonic acid and ammonia. In a similar manner, cyanate of methyl, ethyl, amyl, allyl, and phenyl, furnish carbonic acid, and, respectively, methylamine, ethylamine, amylamine, allylamine, and phenylamine :



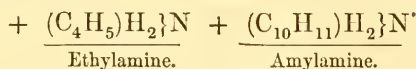
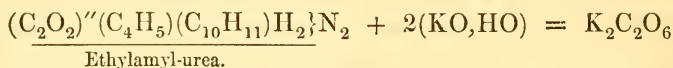
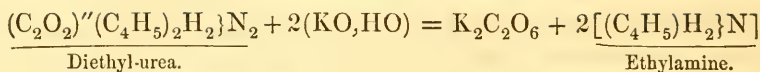
By submitting, at proper temperatures, cyanate of ethyl to the action of ethylate of potassa instead of the hydrate, bases of a higher degree of substitution have been obtained. Cyanate of ethyl thus treated furnishes triethylamine :



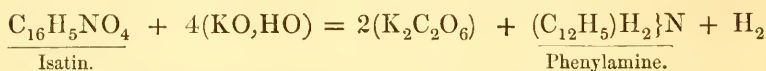
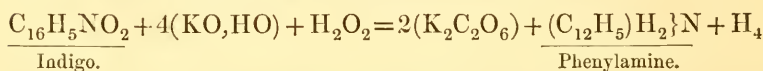
Since the ureas are simply formed by the association of the cyanates with ammonia, it is obvious that their decomposition by the hydrated alkalies must yield ammonia, together with the products of the transformation of the cyanates :



Diethyl-urea thus treated, furnishes carbonate of potassium and 2 equiv. of ethylamine ; ethyl-amyl-urea carbonate, 1 equiv. of ethylamine, and 1 equiv. of amylamine.



In a similar manner indigo and isatin are converted by fusion with the hydrated alkalies into phenylamine, the only difference being the simultaneous evolution of hydrogen gas.



Quinine, cinchonine, and strychnine, when distilled with the hydrated alkalies, furnish leucoline; but the processes cannot be expressed by simple equations, since other products are simultaneously formed. Thus, the distillation of cinchonine furnishes, together with leucoline, lepidine and the pyridine-bases, up to collidine.

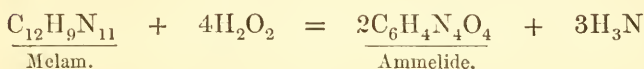
The same remark applies to the transformation of piperine into piperylamine, of caffeine into methylamine, and of morphine, codeine, and narcotine, into bases which are as yet scarcely examined.

Not less complicated are the decompositions of horn, and animal substances in general, under the influence of the fusing hydrated alkalies, which give rise to the formation of glycocine $\text{C}_4\text{H}_5\text{NO}_4$, leucine $\text{C}_{12}\text{H}_{13}\text{NO}_4$, tyrosine $\text{C}_{18}\text{H}_{11}\text{NO}_6$ and even amylamine $\text{C}_{10}\text{H}_{13}\text{N}$.

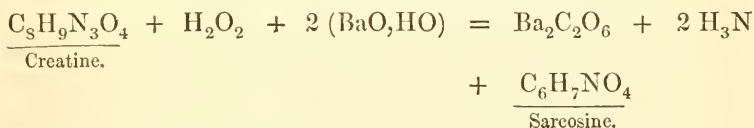
The combinations of the aldehydes with bisulphite of ammonium, when submitted to the action of the hydrated alkalies (soda-lime), also yield bases. The compound of aldehyde (*par excellence*), $\text{C}_4\text{H}_4\text{O}_2$, is thus converted into dimethylamine $\text{C}_4\text{H}_7\text{N}$; that of cœnanthyl-aldehyde $\text{C}_{14}\text{H}_{14}\text{O}_2$, into tricaproylamine $\text{C}_{36}\text{H}_{39}\text{N}$, that of cinnamyl-aldehyde $\text{C}_{18}\text{H}_8\text{O}_2$, into triphenylamine $\text{C}_{36}\text{H}_{15}\text{N}$. These processes cannot be represented by a general equation, since a glance at the formulæ shows that the relation in

which the products stand to each other, differs from the relation which obtains between the mother-compounds.

On the other hand, the formation of the bases furnished by the destructive distillation of sulphocyanide of ammonium, may be readily represented in formulæ. Among the products of this process, an amorphous body, melam, $C_{12}H_9N_{11}$, is found, which by the assimilation of more or less water, yields the three remarkable bases, melamine, ammeline, and ammelide, which are particularly interesting as the first basic compounds artificially produced in the laboratory.

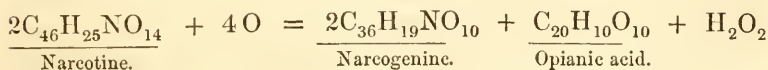
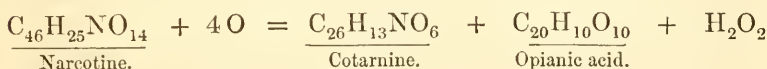


Among the bases formed by the action of the alkalies upon nitrogenous bodies, sarcosine has lastly to be mentioned, which is produced by merely boiling creatine with baryta.

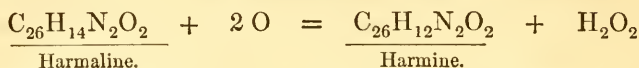


Compared with the basic products resulting from destructive distillation, the number of bases obtained by ordinary processes of oxidation is insignificant.

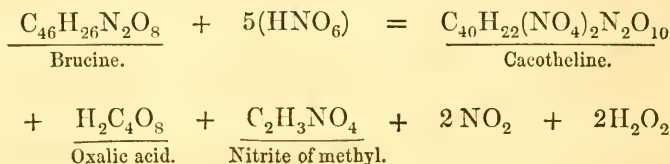
Cotarnine and narcogenine are basic products of oxidation of narcotine, obtained together with opianic acid, by the action of binoxide of manganese and sulphuric acid, or of dichloride of platinum.



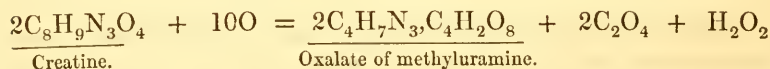
Harmine exists ready formed in the seeds of *Peganum Harmala*, but is also obtained by the oxidation of harmaline.



The action of strong nitric acid upon brucine, gives rise to the formation of cacotheline, a nitrobase, oxalic acid and nitrite of methyl being simultaneously produced.



Creatine when submitted to the action of oxide of mercury, is transformed into oxalate of methyluramine, carbonic acid and water.



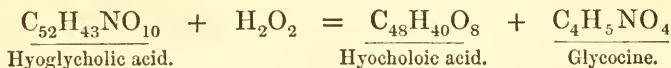
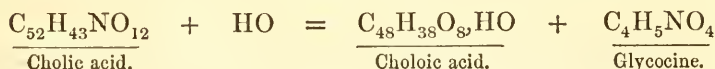
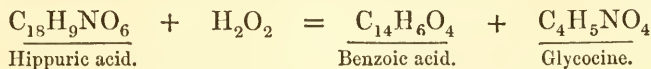
The formation of the bases $(\text{C}_{2n}\text{H}_{(2n+3)})\text{N}$, and of several other series, from the natural alkaloids, by dry distillation, or by the action of the hydrated alkalies, has been already mentioned. This transformation often appears to succeed more readily after the natural alkaloids have been previously oxidized by nitric acid. The volatile bases are then frequently expelled by merely boiling the product with potassa.

Organic bases have been observed to be formed in a variety of processes of putrefaction and fermentation. Thus, the putrefaction of wheaten flour gives rise to the formation of trimethylamine, ethylamine, and amylamine. The former base is also found in putrefied urine, and in considerable quantities in the liquor of salt herrings. In the putrefactive decomposition of flesh, lastly, a portion of the nitrogen appears to be eliminated in the form of organic bases.

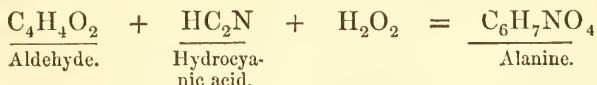
In concluding this section, a few processes may be briefly mentioned which have furnished important sources of organic bases, but can as yet scarcely be regarded from a general point of view.

Glycocine (acetic acid), the formation of which from

chloracetic and bromacetic acid, has been pointed out, was originally obtained by the action of sulphuric acid on gelatine. It is also produced by the action of acids upon hippuric and cholic acids

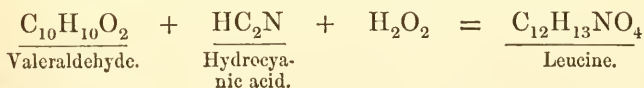


Alanine (propionamic acid) owes its origin to a most remarkable process, viz., the action of hydrocyanic acid upon aldehyde.

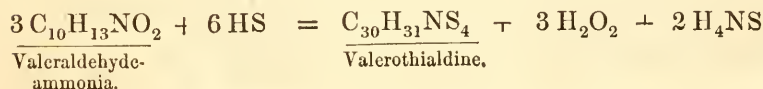
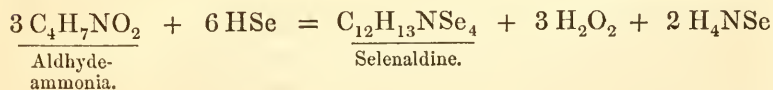
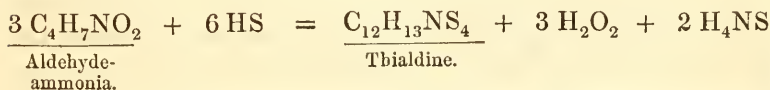


Probably it will be also formed by the action of chloropropionic acid upon ammonia.

Valeraldehyde submitted to the action of hydrocyanic acid, gives rise to the formation of leucine.

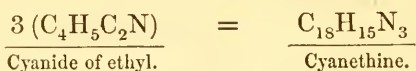


The aldehydes are also convertible into bases, by the action of sulphuretted or selenetted hydrogen, upon their ammonia-compounds.



More isolated still are the reactions which give rise to the formation of cyanethine, of acediamine, and of cyanoline.

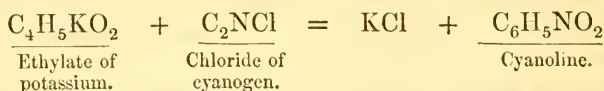
The former is produced by submitting cyanide of ethyl to the action of potassium, when the cyanide is simply polimerized.



Acediamine owes its origin to the action of hydrochloric acid upon acetamide.



Cyanoline, lastly, is formed by the action of chloride of cyanogen upon ethylate of potassium.



Cyanoline is isomeric with cyanate of ethyl.

Allusion has already been made to a numerous group of bases, produced by the substitution of chlorine, bromine, iodine, and hyp硝酸 acid, for hydrogen in the normal derivatives of ammonia. They are generally less basic than the mother-compounds, and sometimes, when the substitution has gone rather far, they are actually neutral bodies. Numerous derivatives of the organic bases have been obtained, moreover, by simple assimilation of iodine or cyanogen. As illustrations of these several classes, the derivatives of phenylamine and of codeine may be quoted.

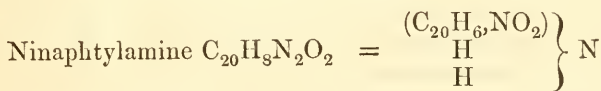
Phenylamine	$\text{C}_{12}\text{H}_7\text{N}$
Chlorphenylamine	$\text{C}_{12}(\text{H}_6\text{Cl})\text{N}$
Dichlorphenylamine	$\text{C}_{12}(\text{H}_5\text{Cl}_2)\text{N}$
Trichlorphenylamine	$\text{C}_{12}(\text{H}_4\text{Cl}_3)\text{N}$ (neutral)
Bromphenylamine	$\text{C}_{12}(\text{H}_6\text{Br})\text{N}$
Dibromphenylamine	$\text{C}_{12}(\text{H}_5\text{Br}_2)\text{N}$

Tribromphenylamine	$C_{12}(H_4Br_3)N$ (neutral)
Chlorodibromphenylamine	$C_{12}(H_4ClBr_2)N$ (neutral)
Iodphenylamine	$C_{12}(H_6I)N$
Nitrophenylamine	$C_{12}(H_6, NO_4)N$
Dinitrophenylamine	$C_{12}(H_5[NO_4]_2)N$ (neutral)
Trinitrophenylamine	$C_{12}(H_4[NO_4]_3)N$ (neutral)
Cyanphenylamine	$C_{12}H_7N, C_2N$

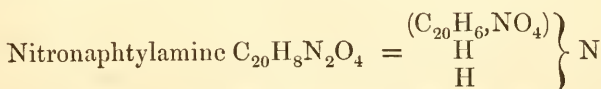
Codeine	$C_{36}H_{21}NO_6$
Chlorocodeine.	$C_{36}(H_{20}Cl)NO_6$
Bromcodeine.	$C_{36}(H_{20}Br)NO_6$
Tribromcodeine.	$C_{36}(H_{18}Br_3)NO_6$
Triiodocodeine	$C_{36}H_{21}NO_6, I_3$
Nitrocodeine.	$C_{36}(H_{20}NO_4)NO_6$
Dicyanocodeine	$C_{36}H_{21}NO_6, 2 C_2N$

In most cases these derivatives are formed by the direct action of chlorine, bromine, iodine, cyanogen and nitric acid, upon the normal bases. In some instances they are obtained by indirect processes, from other substituted compounds. Thus isatin, when distilled with potassa, is converted into phenylamine; chlorisatin and bromisatin, dichlorisatin and dibromisatin, when submitted to a similar treatment, yield respectively, chlorphenylamine and bromphenylamine, dichlorphenylamine and dibromphenylamine. Nitrobenzol, when acted upon by reducing agents, furnishes phenylamine; dinitrobenzol is converted into nitrophenylamine.

In addition to the bases in which we assume the elements of hyponitric acid to replace the hydrogen of the radical, there exists another group, only recently discovered, in which the hydrogen of the radical is replaced by binoxide of nitrogen. Thus dinitronaphthalin yields by reduction—



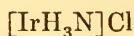
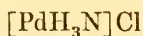
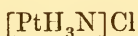
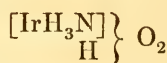
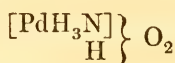
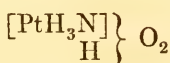
instead of



Metalamines.

Closely connected with the substances, discussed in the previous sections, are two classes of bodies derived from ammonia and from oxide of ammonium, by the substitution of metallic elements for hydrogen. The metallic ammonia-derivatives are all neutral, and will therefore be considered under the head of amides. Here we have only briefly to notice a group of metallic derivatives of hydrated oxide of ammonium, greatly resembling in their general characters the organic bases derived from oxide of ammonium. They differ, however, essentially from the latter, inasmuch as there is only one equivalent of hydrogen replaced in these bodies, whilst the organic ammonium-bases no longer contain any unreplaced ammonium-hydrogen.

The metals, which appear to be most inclined to enter into such combinations, are the several members of the platinum group. The compound metals, platammonium, palladammonium and iridammonium, have as yet been chiefly studied in their saline combinations; even the hydrated oxides being but imperfectly known.

Chlorides.*Hydrated Oxides.*

The compounds belonging to this group are formed by the action of ammonia upon the protochlorides (in general the salts corresponding to the protoxides) of platinum, palladium, and iridium. The chlorides thus obtained may be converted into sulphates, nitrates, oxalates, etc., by treatment with the corresponding silver-compounds; the hydrated oxides, lastly, are liberated by submitting the sulphates to the action of baryta, or, better, the chlorides to the action of oxide of silver.

On treating the protochlorides of the above metals with organic monamines, corresponding bodies are formed, containing, in addition to the metal replacing hydrogen, an organic molecule, performing a similar function. We obtain, in this manner, the chlorides of

Palladethyl-ammonium	$[\text{Pd}(\text{C}_4\text{H}_5)\text{H}_2\text{N}]\text{Cl}$ and
Palladophenyl-ammonium	$[\text{Pd}(\text{C}_{12}\text{H}_5)\text{H}_2\text{N}]\text{Cl}$

Similar salts are produced by boiling the platinum-salts of several organic bases with water, when hydrochloric acid separates and chlorine is eliminated in secondary products of decomposition. Thus the double salt of dichloride of platinum and hydrochlorate of pyridine yields the

Chloride of Platopyridyl-ammonium $[\text{Pt}(\text{C}_{10}\text{H}_5)'''\text{N}]\text{Cl}$

Under the influence of chemical agents, these metalammonium-compounds are converted into substances of a more complicated constitution. Chloride of platammonium, when suspended in water and submitted to the action of chlorine, is transformed into a new salt, PtH_3NCl_2 , differing from the former by containing an additional equivalent of chlorine. By continued boiling with nitrate of silver, this new chloride is converted into a nitrate, from which ammonia separates a crystalline substance of the composition PtH_5NO_4 .

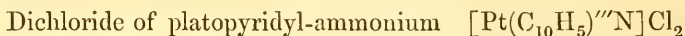
These formulæ have received different interpretations: whilst some Chemists see in the new compounds a higher chloride and a higher oxide of platammonium,

Dichloride of platammonium	$[\text{PtH}_3\text{N}]''\text{Cl}_2$
Dioxide of platammonium	$[\text{PtH}_3\text{N}]''\left\{ \begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{O}_4$

others object to this view that a dichloride of ammonium, H_4NCl_2 , has never been obtained, and, guided by the fact that the new compound is proved, by its deportment with silver-salts, to contain the chlorine in two different forms, they assume that the hydrogen in ammonium may be replaced, not only by metals, but even by chlorides and oxides of metals. The bodies in question would thus become:

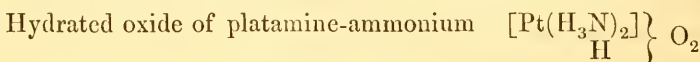
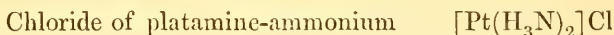
Chloride of chlorplatammonium	$[(\text{PtCl})'\text{H}_3\text{N}]\text{Cl}$, and
Oxide of oxyplatammonium	$[(\text{PtO})'\text{H}_3\text{N}]\left\{ \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\} \text{O}_2 + \text{HO}$

Whatever view may be taken regarding these substances, it is obvious that some of the salts, obtained by boiling the platinum-compounds of several of the organic bases, belong to the same class. Thus the platinum-salt of pyridine furnishes, together with the chloride of platopyridyl-ammonium, a second compound, containing twice the quantity of chlorine present in the former salt :

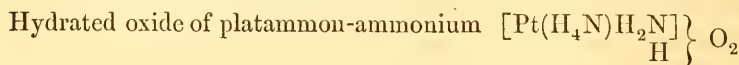
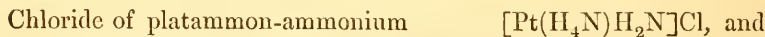


Not less complicated appears the constitution of a series of derivatives obtained from the chloride of platammonium by the action of ammonia. This process gives rise to the formation of prismatic crystals, $\text{PtH}_6\text{N}_2\text{Cl}$, from which, by treatment with silver-salts, a series of well-defined saline bodies, $\text{PtH}_6\text{N}_2\text{X}$, and, lastly, by the action of oxide of silver, an excessively caustic oxide, $\text{PtH}_6\text{N}_2\text{O}, \text{HO}$ may be obtained.

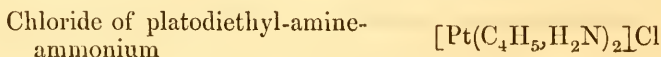
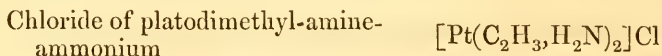
These substances exhibit considerable analogy with those derivatives of the organic bases, which in a preceding section we have designated as *diamine-ammonium-compounds*.



But they may also be viewed as ordinary ammonium-compounds if we assume that the hydrogen in ammonium is capable of being replaced by ammonium itself. The compounds in question would thus become :



If protochloride of platinum be treated with an excess of methylamine or ethylamine, until the insoluble compounds produced in the first stage of the process, are redissolved, the corresponding methyl- and ethyl-derivatives are formed :



Two similar palladium-compounds are produced by the action of ethylamine on chloride of palladammonium and upon protochloride of palladium :

Chloride of palladethyl-amine-ammonium $[\text{Pd}(\text{C}_4\text{H}_5, \text{H}_2\text{N}, \text{H}_3\text{N})]\text{Cl}$

Chloride of palladodiethyl-amine-ammonium $[\text{Pd}(\text{C}_4\text{H}_5, \text{H}_2\text{N})_2]\text{Cl}$

The action of chlorine upon the chloride of platamine-ammonium is similar to that on the chloride of platammonium; it gives rise also to the formation of a compound differing from the original substance by an additional equivalent of chlorine.

The views taken by Chemists respecting the chlorinected chloride of platammonium, are of course equally applicable to the analogous derivative of the platamine-ammonium-series. This derivative may accordingly be considered as

Dichloride of platamine-ammonium $[\text{Pt}(\text{H}_3\text{N})_2]''\text{Cl}_2$, or as

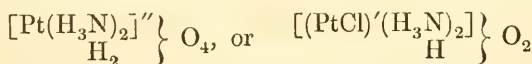
Chloride of chlorplatamine-ammonium $[(\text{PtCl})'(\text{H}_3\text{N})_2]\text{Cl}$

The latter view is supported by the observation that silver-salts remove from this compound, at once or after a short boiling, only half the chlorine, the second half being eliminated, with considerable difficulty, after protracted ebullition. The removal of 1 equiv. of chlorine, by means of nitrate of silver, gives rise to the formation of a well-defined nitrate, which may be also obtained by the action of nitric acid upon the chloride of platammonium. According as we take the former or the latter view, this nitrate must be regarded as

Chloro-nitrate of platamine-ammonium $[\text{Pt}(\text{H}_3\text{N})_2]''\left\{ \begin{smallmatrix} \text{Cl} \\ \text{NO}_6 \end{smallmatrix} \right\}$ or as

Nitrate of chlorplatamine-ammonium $[(\text{PtCl})'(\text{H}_3\text{N})_2]\text{NO}_6$

The corresponding oxide,



has not as yet been formed.

The deportment of mercury-salts with ammonia presents phenomena, strongly resembling those which are observed in the analogous reactions with platinum-salts. When corrosive sublimate is added to a boiling solution of chloride of ammonium, until the precipitate first formed, is redissolved, the liquid deposits on cooling, a dodecahedral salt, containing $\text{HgCl}, \text{H}_3\text{N}$, which may be viewed as chloride of mercurammonium $[\text{HgH}_3\text{N}]\text{Cl}$. Gently heated, these crystals lose half their ammonia, being converted into $2\text{HgCl}, \text{H}_3\text{N}$, or a double salt of chloride of mercurammonium with chloride of mercury $[\text{HgH}_3\text{N}]\text{Cl}, \text{HgCl}$. Analogous iodides exist, but neither the sulphate, the nitrate, nor the corresponding oxide have hitherto been produced.

The *white precipitate* produced by adding an excess of ammonia to a solution of corrosive sublimate, contains $\text{HgCl}, \text{HgH}_2\text{N}$. It may be viewed as chloride of dimercurammonium $[\text{Hg}_2\text{H}_2\text{N}]\text{Cl}$. If the chloride of mercury be used in excess, the precipitate has the composition of a double salt of the chlorides of dimercurammonium and mercury $3\text{HgCl}, \text{HgH}_2\text{N} = [\text{Hg}_2\text{H}_2\text{N}]\text{Cl}, 2\text{HgCl}$. In a similar manner the yellow body $2\text{HgO}, \text{HgCl}, \text{HgH}_2\text{N}$, formed by continued washing of the *white precipitate* with water or dilute alkali, may be regarded as a double salt of chloride of dimercurammonium and oxide of mercury $[\text{Hg}_2\text{H}_2\text{N}]\text{Cl}, 2\text{HgO}$. This compound admits, however, also of another interpretation.

Bromide of mercury gives rise to the formation of analogous compounds. The so-called basic ammonio-nitrate of mercury $\text{HgNO}_6, 2\text{HgO}, \text{H}_3\text{N}$, when boiled with ammonia and nitrate of ammonium, is converted into a yellow crystalline salt $\text{HgNO}_6, \text{HgO}, \text{H}_3\text{N}$, which may be viewed as hydrated nitrate of dimercurammonium $[\text{Hg}_2\text{H}_2\text{N}]\text{NO}_6 + \text{HO}$. Other compounds of this series, and especially the oxide corresponding to the *white precipitate*, are not known.

The brown nitride of mercury Hg_3N , which is formed by the action of ammonia on yellow oxide of mercury, does not combine with acids, and must, therefore, be viewed as trimercuramide. On the other hand, the basic ammonio-nitrate of mercury, to which allusion has already been made, might be considered as hydrated nitrate of trimercurammonium $[\text{Hg}_3\text{HN}]\text{NO}_6 + 2\text{HO}$.

There exists lastly, a large group of ammoniacal mercury-salts, which may be interpreted as tetramercurammonium-compounds.

Yellow protoxide of mercury, when treated with ammonia, furnishes a compound of the same colour, which dried at the

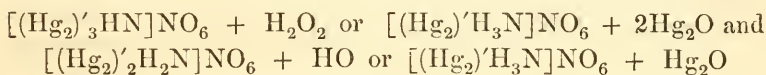
common temperature in the air, contains $4\text{HgO}, \text{H}_3\text{N} + \text{H}_2\text{O}_2$. Exposed for some time over sulphuric acid, it loses 2 equivs. of water, and lastly becomes $3\text{HgO}, \text{HgH}_2\text{N}$, when dried at 130° . This body is a powerful base, expelling ammonia from its compounds, and forming, with the acids, well-defined salts capable of double decomposition. The free base may be boiled with the alkalis without undergoing any change. The compound in question may be viewed as hydrated oxide of tetramercurammonium $\left[\begin{smallmatrix} \text{Hg}_4\text{N} \\ \text{H} \end{smallmatrix} \right] \left. \vphantom{\begin{smallmatrix} \text{Hg}_4\text{N} \\ \text{H} \end{smallmatrix}} \right\} \text{O}_2 + \text{HO}$. The salts of this base, have the general formula $[\text{Hg}_4\text{N}]\text{X} + \text{H}_2\text{O}_2$. It deserves to be noticed that these salts retain the 2 equivs. of water which were originally present in the oxide, and that this water cannot be separated without destroying them. This observation appears in some measure to militate against the tetramercurammonium-theory. In fact, the substances in question, may be also considered as salts of dimercurammonium combined with protoxide of mercury. Indeed, a salt, which has just been represented as a compound of chloride of dimercurammonium with protoxide of mercury, may as rightly be regarded as hydrated chloride of tetramercurammonium $[\text{Hg}_2\text{H}_2\text{N}]\text{Cl} + 2\text{HgO} = [\text{Hg}_4\text{N}]\text{Cl} + \text{H}_2\text{O}_2$.

Less doubtful appears the tetramercurammonic character in the red body, which is formed by the action of heat upon the *white precipitate*. This compound contains $2\text{HgCl}, \text{Hg}_3\text{N}$, and may be considered as a double salt of chloride of tetramercurammonium and chloride of mercury $[\text{Hg}_4\text{N}]\text{Cl} + \text{HgCl}$.

Suboxide of mercury gives rise to ammoniacal compounds, perfectly similar to those which have been mentioned. They are less known.

The action of ammonia upon calomel, produces the compounds $\text{Hg}_2\text{Cl}, \text{H}_3\text{N}$ and $2\text{Hg}_2\text{Cl}, \text{H}_3\text{N}$, which may be viewed as $[(\text{Hg}_2)'\text{H}_3\text{N}]\text{Cl}$ and $[(\text{Hg}_2)'\text{H}_3\text{N}]\text{Cl}, \text{Hg}_2\text{Cl}$, assuming that $(\text{Hg}_2)'$ performs the functions of 1 equiv. of hydrogen.

In conclusion, the so-called *Mercurius solubilis Hahnemanni*, may be mentioned. The composition of this compound is uncertain. According to some Chemists, it contains $2\text{Hg}_2\text{O}, \text{Hg}_2\text{NO}_6, \text{H}_3\text{N}$, according to others $\text{Hg}_2\text{O}, \text{Hg}_2\text{NO}_6, \text{H}_3\text{N}$. Adopting the mercurammonium-theory these compounds may be received as—



If the view taken of the constitution of the ammoniacal salts of platinum and mercury be extended to the combinations of ammonia with other metals, we arrive at an almost endless series of metalammonium-compounds, amongst which the combinations of copper, zinc, cadmium, nickel, and silver, are particularly conspicuous. As examples, the following may be quoted:—

Ammoniacal subchloride of copper	$\text{Cu}_2\text{Cl}, \text{H}_3\text{N} = [(\text{Cu}_2)'\text{H}_3\text{N}] \text{Cl}$	Chloride of cupros-am- monium
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Ammoniacal protochloride of copper	$\text{CuCl}, \text{H}_3\text{N} = [\text{CuH}_3\text{N}] \text{Cl}$	Chloride of cupr-ammo- nium
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Ammoniacal chloride of zinc	$\text{ZnCl}, \text{H}_3\text{N} = [\text{ZnH}_3\text{N}] \text{Cl}$	Chloride of zinc-ammo- nium.
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Ammoniacal chloride of cadmium	$\text{CdCl}, \text{H}_3\text{N} = [\text{CdH}_3\text{N}] \text{Cl}$	Chloride of cadm-ammo- nium
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Ammoniacal chloride of uranium	$\text{UCl}, \text{H}_3\text{N} = [\text{UH}_3\text{N}] \text{Cl}$	Chloride of uran-ammo- nium
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Metallic salts, containing more than one equivalent of ammonia, appear less simple when regarded from this point of view. The ammon-ammonium cannot then be dispensed with.

Diammoniacal protochloride of copper	$\text{CuCl}, 2\text{H}_3\text{N} = [\text{Cu}(\text{H}_4\text{N})\text{H}_2\text{N}] \text{Cl}$	Chloride of cupr-ammon- ammonium
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Diammoniacal chloride of zinc	$\text{ZnCl}, 2\text{H}_3\text{N} = [\text{Zn}(\text{H}_4\text{N})\text{H}_2\text{N}] \text{Cl}$	Chloride of zinc-ammon- ammonium
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Diammoniacal iodide of nickel	$\text{NiI}, 2\text{H}_3\text{N} = [\text{Ni}(\text{H}_4\text{N})\text{H}_2\text{N}] \text{I}$	Iodide of nickel-ammon- ammonium
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Diammoniacal nitrate of silver	$\text{AgNO}_6, 2\text{H}_3\text{N} = [\text{Ag}(\text{H}_4\text{N})\text{H}_2\text{N}] \text{NO}_6$	Nitrate of argent-am- mon-ammo- nium
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and in a similar manner—

Triammoniacal protochloride of copper	$\text{CuCl}, 3\text{H}_3\text{N} = [\text{Cu}(\text{H}_4\text{N})_2\text{HN}]\text{Cl}$	Chloride of cupro-diam- mon-am- monium
Triammoniacal chloride of nickel	$\text{NiCl}, 3\text{H}_3\text{N} = [\text{Ni}(\text{H}_4\text{N})_2\text{HN}]\text{Cl}$	Chloride of nickel-diammon- ammonium
Triammoniacal chloride of cobalt	$\text{CoCl}, 3\text{H}_3\text{N} = [\text{Co}(\text{H}_4\text{N})_2\text{HN}]\text{Cl}$	Chloride of cobalt-diammon- ammonium
Triammoniacal nitrate of silver	$\text{AgNO}_3, 3\text{H}_3\text{N} = [\text{Ag}(\text{H}_4\text{N})_2\text{HN}]\text{NO}_3$	Nitrate of ar- gent-diam- mon-am- monium

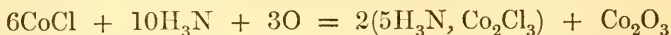
It cannot be denied that these interpretations are somewhat forced. There are, moreover, compounds of metallic salts with ammonia in proportions which altogether defy the elasticity of the ammonium-type. Considering, lastly, that most of the previously mentioned ammoniacal salts are extremely unstable—many losing their ammonia by simple exposure to the atmosphere—and that in scarcely any case a corresponding oxide has been obtained, it becomes obvious that in the majority of these substances, the assumption of a metalammonie constitution is scarcely justified.

We terminate this imperfect sketch of the metalammonium-combinations by briefly noticing a peculiar class of compounds which has attracted considerable attention during the last few years, but the history of which, notwithstanding many excellent researches, is still far from being finally elaborated.

When ammoniacal solutions of cobalt-salts are left in contact with atmospheric air, we find that in addition to the group represented by the triammoniacal chloride of cobalt, which has just been mentioned, a series of other salts is formed, generally well crystallised and remarkable for the number of ammonia-equivalents which appear to be joined in one molecule.

The investigation of these interesting compounds being still incomplete, we must limit ourselves to enumerate the formulæ given by their discoverers, and to state the conditions under which they have been formed.

Roseo-cobalt-salts are formed by the action of air at a *low* temperature on the ammoniacal solution of a cobalt-salt. The chloride yields in this manner the compound, $5\text{H}_3\text{N}, \text{Co}_2\text{Cl}_3$.



Nitrate of cobalt, similarly treated, yields $5\text{H}_3\text{N}, \text{Co}_2(\text{NO}_6)_3$. The sulphate exhibits an analogous deportment. Preserved for some time, the roseo-cobalt-salts are transformed into

Purpureo-cobalt-salts, which may be more readily obtained by boiling the solutions of roseo-cobalt-salts, or by boiling simply the ammoniacal solution of a cobalt-salt in contact with air. The ratio of cobalt and nitrogen in the purpureo-cobalt-salts is the same as in the roseo-cobalt-salts, from which they differ, however, in form and properties, often also in the proportion of acid-equivalents which the compound ammonia-molecule in these salts is capable of fixing. Treatment of the sulphate with baryta, furnishes a powerfully alkaline solution, which constitutes the free base of the series. This base is very readily decomposed. The platinum-salt contains $5\text{H}_3\text{N}, \text{Co}_2\text{Cl}_3, 2\text{PtCl}_2$.

Luteo-cobalt-salts are generated apparently under the same circumstances which give rise to the previous classes. Their preparation is very uncertain, and appears to succeed best when a solution of chloride or sulphate of cobalt, supersaturated with ammonia and mixed with an excess of sal-ammoniac is exposed to the air. The luteo-cobalt-salts contain :

Chloride . . .	$6\text{H}_3\text{N}, \text{Co}_2\text{Cl}_3$
Platinum-salt . .	$6\text{H}_3\text{N}, \text{Co}_2\text{Cl}_3, 3\text{PtCl}_2 + 3\text{H}_2\text{O}_2$
Nitrate . . .	$6\text{H}_3\text{N}, \text{Co}_2(\text{NO}_6)_3$

The base of this series has been likewise isolated: it cannot, however, be obtained in the dry state.

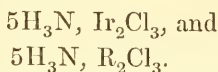
Roseo- and purpureo-cobalt-salts, or ammoniacal solutions of cobalt-salts, when submitted to the action of nitrous acid are converted into

Xantho-cobalt-salts, which appear to contain the elements of binoxide of nitrogen :

Chloride . . .	$\text{NO}_2, 5\text{H}_3\text{N}, \text{Co}_2\text{OCl}_2 + \text{HO}$
Platinum-salt . .	$\text{NO}_2, 5\text{H}_3\text{N}, \text{Co}_2\text{OCl}_2, 2\text{PtCl}_2 + \text{HO}$

The theory of these compounds is not yet established.

The sesqui-chlorides of iridium and rhodium unite with ammonia to form compounds of the formulæ,



Corresponding sulphates and nitrates have been formed. The chlorides, when submitted to the action of oxide of silver, yield, with difficulty, alkaline liquids exhibiting but very little stability. The constitution of these compounds appears to be the same as that of the roseo-cobalt-salts.

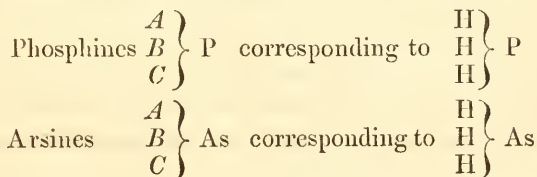
Basic Derivatives of Phosphoretted, Antimonetted, and Arsenetted Hydrogen.

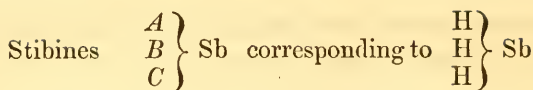
It is impossible to leave the history of the basic nitrogen-compounds, without alluding briefly to a series of basic bodies containing phosphorus, arsenic, and antimony, in the place of nitrogen, which exhibit both in constitution and chemical deportment, a remarkable analogy with the corresponding terms of the nitrogen-series.

In the preceding part of this discourse, we have endeavoured to refer the molecular construction of the nitrogen-bases to ammonia (ammonia-type), or hydrated oxide of ammonium (water-type); in a similar manner, the substances which we have now to mention, may be referred to the terhydrides of phosphorus, arsenic and antimony corresponding to ammonia, and to a series of hypothetical compounds, containing phosphorus, arsenic and antimony, corresponding to hydrated oxide of ammonium, and consequently constructed upon the water-type. The substances derived from the analogues of ammonia are designated by the terms phosphines, arsines and stibines, and those derived from hydrated oxide of ammonium, as phosphonium-, arsonium-, and stibonium-compounds.

The classes in question may be represented by the following general formulæ:

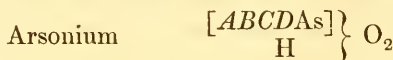
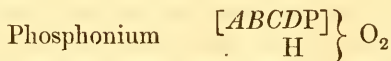
Compounds constructed on the Ammonia-type.





Compounds constructed on the Water-type.

Hydrated oxides of—



On comparing phosphoretted, arsenetted, and antimonetted hydrogen, with the corresponding nitrogen-compound with ammonia, similarity of composition, attended by similarity of chemical character, appears only in the case of phosphoretted hydrogen, which, like ammonia, is capable of combining with acids. This combining power, however, is very feeble, only a few saline compounds, such as those with hydriodic and hydrobromic acid, and some chlorides, having been as yet obtained. Arsenetted and antimonetted hydrogen, do not combine with acids, they have in fact, nothing in common with ammonia, except analogy of composition.

This want of similarity in chemical deportment, is, however, far less apparent in the derivatives which we conceive to originate from the hydrides by the substitution of alcohol-radicals for their hydrogen. These substitutions give rise to the formation of phosphorus-, arsenic-, and antimony-compounds, exhibiting a combining tendency for acids, scarcely inferior to that of their nitrogen-analogues; by the transition of these compounds into bodies constructed upon the water-type, even the last discrepancies have disappeared, the ammonium-, phosphonium-, arsonium-, and stibonium-derivatives, presenting the most perfect analogy in their chemical deportment.

The basic character of phosphoretted hydrogen, scarcely perceptible in the formation of a few feeble saline compounds, is so much enhanced by the substitution of methyl or ethyl for its hydrogen, that the substitution-products, thus generated, acquire the properties of powerful bases, manifested particularly in the formation of well-characterized salts and platinum-compounds. They have, however, no action on vegetal colours.

The trimethylated and triethylated derivatives of arsenetted and antimonetted hydrogen, resemble their analogues in the phosphorus-series, in their mode of generation and in their constitution; they differ, however, considerably in their chemical deportment, inasmuch as all attempts to produce the compounds, corresponding to the ammonia-salts, have hitherto entirely failed.

On further comparing the nitrogen-, phosphorus-, arsenic-, and antimony-bases, we find that the electro-positive character of these compounds rises from the nitrogen-group towards the antimony-series; acquiring its greatest intensity in trimethylstibine and triethylstibine. Whilst trimethylamine and triethylamine, for instance, are incapable of entering into direct combination with oxygen, chlorine, bromine, etc., we find in the corresponding compounds of phosphorus, arsenic, and antimony so great an attraction for these elements, that combination takes place at the common temperature, frequently with explosive violence. This extraordinary attraction for the oxygenides constitutes the most characteristic mark of distinction between the nitrogen-bases, on the one hand, and the phosphorus-, arsenic- and antimony-bases on the other. In the arsenic- and antimony-compounds this combining tendency is so powerful that they decompose the strongest acids with assimilation of the electro-negative constituent; and this explains sufficiently why these substances appear incapable of forming saline compounds with the acids. In the phosphorus-bases this combining tendency is less energetic; they furnish both salts with the acids, and direct combinations with their oxygenides. The phosphorus-bases accordingly form the link of connection between the nitrogen-group and the arsenic- and antimony-series.

This gradation is no longer perceptible in the substances analogous to hydrated oxide of ammonium. In these remarkable bodies the analogy of composition induces an almost absolute identity of chemical deportment; and we are surprised to find elements so dissimilar as nitrogen, phosphorus, arsenic, and antimony involved in the formation of compounds so like each other, and which, in fact, we can distinguish only by their destruction.

In accordance with the experience acquired in the nitrogen-series, we naturally expect to find, in addition to the bodies corresponding to the monamines, and which we designate as monophosphines, monarsines, and monostibines, a class of compounds representing the polyamines of the nitrogen-group. It may at once be stated that this class has as yet but very few representatives.

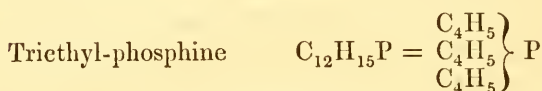
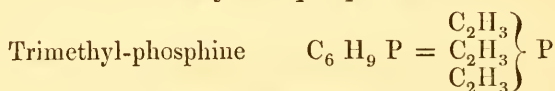
Again, we may distinguish primary, secondary, and tertiary monophosphines, monarsines, etc. As yet chemists have succeeded only in producing the compounds corresponding to the tertiary monamines. All attempts to produce analogues of the primary and secondary monamines have hitherto entirely failed.

In the following tables we have united the principal terms of the several groups to which we have alluded :

PHOSPHORUS SERIES.

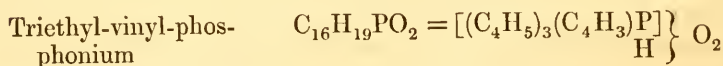
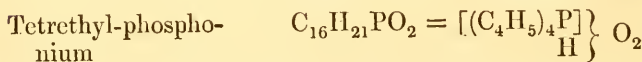
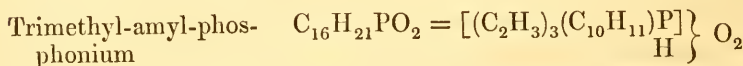
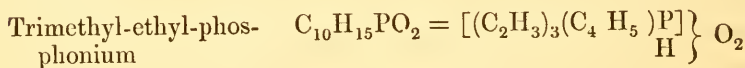
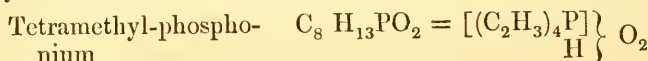
Type Ammonia.

Tertiary Monophosphines.



Type Water.

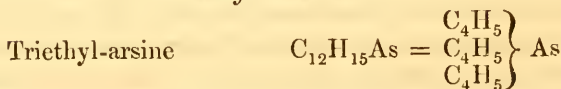
Hydrated oxide of—



ARSENIC SERIES.

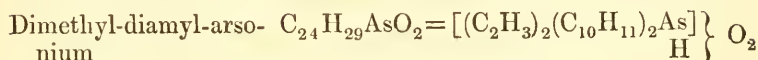
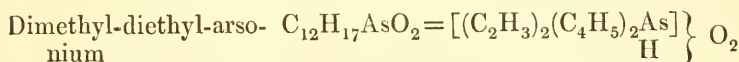
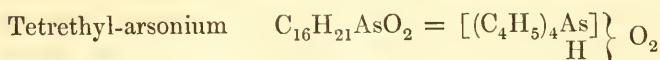
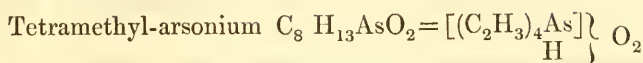
Type Ammonia.

Tertiary Monarsines.



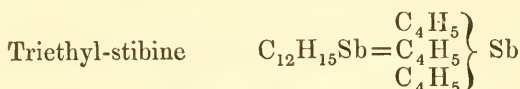
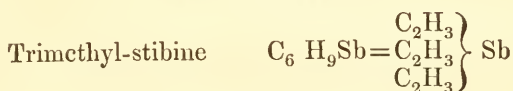
Type Water.

Hydrated oxide of—



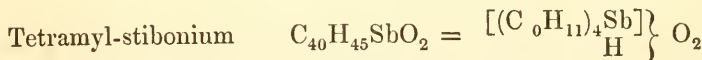
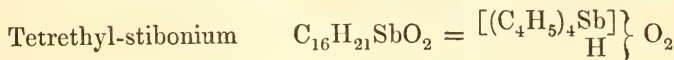
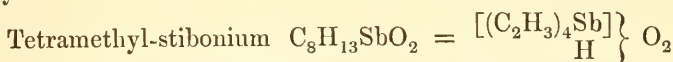
ANTIMONY SERIES.

Type Ammonia.

Tertiary Monostibines.

Type Water.

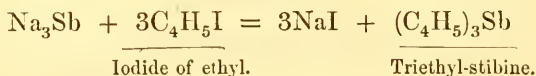
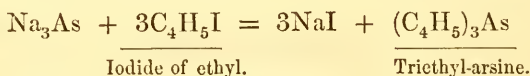
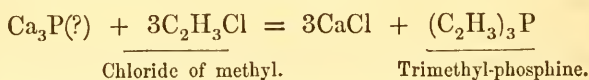
Hydrated oxide of—

*Formation of the Phosphorus-, Arsenic-, and Antimony-Bases.*

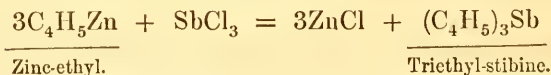
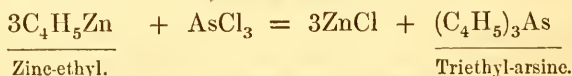
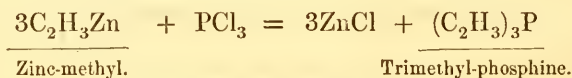
These bodies have not yet been obtained by direct substitution from the hydrides of phosphorus, arsenic, and antimony. The methods hitherto employed for their production essentially consist in submitting a metallic compound of phosphorus, arsenic, or

antimony to the action of the iodides, bromides, and chlorides of the alcohol-radicals; or, *vice versâ*, in treating the metallic compounds of the alcohol-radicals, with the iodides, bromides, and chlorides of phosphorus, arsenic, and antimony.

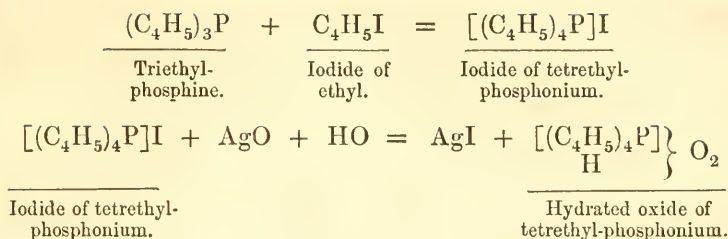
The following equations illustrate the reactions first mentioned. It deserves to be noticed that these processes generally yield only a very uncertain result; other compounds are always simultaneously produced.



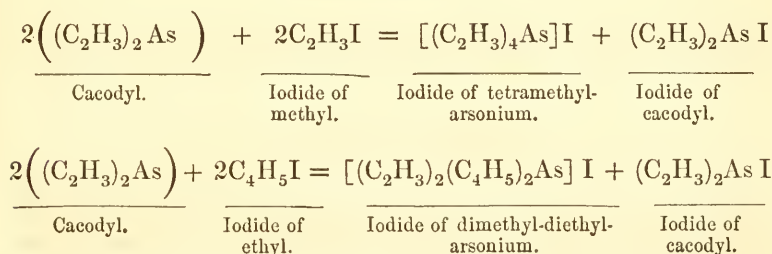
The second reaction furnishes the substances in greater abundance and of remarkable purity.



In order to convert the bodies corresponding to the type ammonia into compounds corresponding to the type water, the former are simply treated with the bromides or iodides of the radicals to be added. Exactly as with the nitrogen-bases a powerful reaction ensues, even at the common temperature, and the bromides and iodides of the newly-formed phosphonium, arsonium, or stibonium are generally precipitated in the crystalline state. From these compounds the hydrated oxides are separated by the action of oxide of silver.



In the arsenic-series, the compounds in question have been also produced by the action of the iodides of the alcohol-radicals on cacodyl.



Metaphosphonium-compounds.

The phosphorus-, arsenic-, and antimony-bases form a series of platinum-compounds remarkable for the facility and beauty with which they crystallize, and presenting great analogy with the platammonium-salts; as yet only the chlorides are examined. On treating an alcoholic solution of triethyl-phosphine, triethyl-arsine, or triethyl-stibine, with dichloride of platinum, the solutions are decolorised and the new chlorides separate in crystals.

The following have been examined:—

Chloride of—

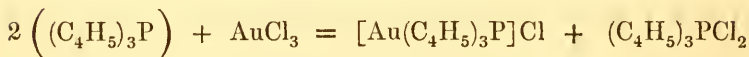
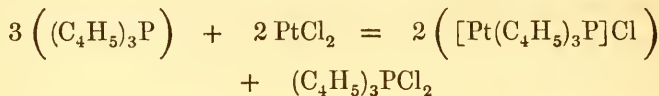
Platotriethyl-phosphonium	$[\text{Pt}(\text{C}_4\text{H}_5)_3\text{P}]\text{Cl}$
Platotriethyl-arsonium	$[\text{Pt}(\text{C}_4\text{H}_5)_3\text{As}]\text{Cl}$
Platotriethyl-stibonium	$[\text{Pt}(\text{C}_4\text{H}_5)_3\text{Sb}]\text{Cl}$

Trichloride of gold produces a series of similar gold-compounds, which are easily obtained in beautiful colourless crystals.

Chlorides of—

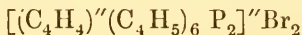
Aurotriethyl-phosphonium	$[\text{Au}(\text{C}_4\text{H}_5)_3\text{P}]\text{Cl}$
Aurotriethyl-arsonium	$[\text{Au}(\text{C}_4\text{H}_5)_3\text{As}]\text{Cl}$
Aurotriethyl-stibonium	$[\text{Au}(\text{C}_4\text{H}_5)_3\text{Sb}]\text{Cl}$

Both the platinum- and gold-compounds are generated with simultaneous formation of the dichlorides of the bases.

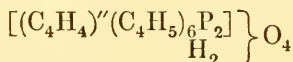


Diphosphonium-compounds.

Recent researches have proved that the chlorides, bromides and iodides of diatomic molecules are capable of combining with 2 equivalents of the monophosphines, giving rise to a new class of phosphorus-bases, analogous to the diammonium-compounds. The only member of this class, as yet examined, is a product of the action of dibromide of ethylene on triethylphosphine. In this reaction a variety of substances are formed, but under certain conditions, the principal product is the bromide of ethylene-hexethyl-diphosphonium.



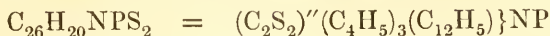
Treated with oxide of silver, this body furnishes a powerfully alkaline liquid, which contains the oxide of the series.



Phosphamines.

By the union of the monamines and monaphosphines of opposite chemical character, a peculiar class of *ureas* has been produced, containing both nitrogen and phosphorus, which may be designated by the above name. The most remarkable term of this class is a

well-defined compound, formed by the action of sulphocyanide of phenyl upon triethylphosphine ; it contains—



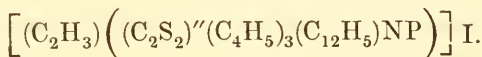
and may be viewed as *urea*, in which the oxygen is replaced by sulphur, the hydrogen by 3 equivs. of ethyl and 1 equiv. of phenyl, whilst phosphorus is substituted for half the quantity of nitrogen. This compound is a well-characterized base, forming definite crystalline salts of the formula—



Even with the iodides of methyl and ethyl, the new urea readily combines, producing with the former, for instance, the compound



In constitution this substance resembles the bodies which, in the nitrogen-series, have been designated as diamine-ammonium compounds.



(To be concluded in our next.)

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.

November 4, 1858,

Dr. H. Bence Jones, Vice-President, in the Chair.

THE following donations were announced :—

“Dr. Stenhouse on Charcoal,” from the Author.

“Proceedings of the Royal Society of Edinburgh,” from the Society.

“Papers read at the Botanical Society of Edinburgh,” by Dr. Lawson, from the Author.

“On the Estimation of the Precious Metals,” by J. Mitchell, from the Author.

“Proceedings of the Academy of Natural Sciences of Philadelphia,” from the Academy.

“Notices of the Proceedings of the Royal Institution, with List of Members,” from the Institution.

“Transactions of the Royal Scottish Society of Arts,” from the Society.

“The Annual Report of the Royal Cornwall Polytechnic Society,” from the Society.

“The Pharmaceutical Journal,” from the Editor.

“The Journal of the Society of Arts,” from the Society.

“The Journal of the Franklin Institute,” from the Institute.

“Report of the Committee appointed to consider the propriety of establishing a degree in Science,” from the University of London.

Mr. James Mason was elected a Fellow of the Society.

Dr. Hofmann gave an account of some new Ureas that he had recently produced.

November 18, 1858.

Dr. G. D. Longstaff in the Chair.

The following donations were announced:—

“Bulletin de la Classe Physico-Mathématique de l'Académie Impériale des Sciences de Saint Petersburg;” “Comptes Rendus of do.,” from the Academy.

“Quarterly Journal of the Geological Society,” from the Society.

“Journal of the Society of Arts,” from the Society.

It was resolved that the names of the following Fellows, whose subscriptions have fallen into arrear, be removed from the List of Fellows of the Chemical Society:—P. E. Coffey, R. D. Kay, W. Crowder, J. C. Shearman, M. L. Phillips, T. Richardson.

The following papers were read:—

“On the analysis of the Water of a Spring at Billingborough in Lincolnshire,” by Mr. Kynaston,

“On Bibromacetic Acid,” by Messrs. Perkin and Duppa.

Dr. Hofmann, on the part of Professor Fritzsche, exhibited some compounds of picric acid with benzine, naphthaline, and other hydrocarbons.

December 2, 1858.

Dr. G. D. Longstaff in the Chair.

The following papers were read:—

“Analysis of the Water of Holywell, North Wales,” by Mr. James Barratt.

“On the relations of the atomic weights of Elements,” by Mr. Mercer.

“On the detection of Alum in Bread,” by Mr. John Horsley.

Dr. Hofmann described a new double salt of iodide and nitrate of silver, obtained by heating recently precipitated iodide of silver in a solution of nitrate of silver in nitric acid.

December 16, 1858.

Dr. Frankland, in the Chair.

The following donations were announced :—

“Journal of the Royal Dublin Society, Vol. I,” from the Society.

“Journal of the Franklin Institute,” from the Institute.

“Journal of the Photographic Society,” from the Society.

“Journal of the Society of Arts,” from the Society.

“Pharmaceutical Journal,” from the Editor.

Alfred Hill, M.D., Sydenham College, Birmingham, was elected a Fellow of the Society.

Mr. E. A. Sansom, 27, Carey Street, was elected an Associate of the Society.

The following papers were read :—

“On some minerals containing Arsenic and Sulphur, from Chili,” by Mr. F. Field.

“On the presence of Ammonia in Ice, and on the action of Ice-water upon Lead,” by Dr. Medlock.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1858.

A

- Acetamide.—Formation of acetamide from acetate of ammonia: by *Dr. Kündig*. *Ann. Ch. Pharm.* cv. 277; *J. pr. Chem.* lxxiv. 128.
- Acetal.—Conversion of aldehyde into acetal: by *A. Wurtz* and *A. Frapolli*. *Compt. rend.* xlvii. 418; *Ann. Ch. Pharm.* cviii. 223.
- Acetates.—On acetate of alumina: by *Ch. Tissier*. *Compt. rend.* xlvii. 931.
- Researches on the acetates of iron: by *A. S. Kestner*. *Compt. rend.* xlvii. 927.
- Preparation of basic acetate of lead: by *F. Rochleder*. *J. pr. Chem.* lxxiv. 28; *J. Pharm.* [3] xxxiv. 240; *Pharm. J. Trans.* xviii. 169.
- On monoacetate of glycol: by *E. Atkinson*. *Phil. Mag.* [4] xvi. 433.
- Acetenamine.—Observations on the composition of formenamine, formylene, acetenamine, acetylene, and several analogous bases: by *S. Cloez*. *Compt. rend.* xlv. 344; *J. pr. Chem.* lxxiv. 84.
- Acetones.—Note on the constitution of the acetones: by *C. Friedel*. *Compt. rend.* xlv. 1013; xlvii. 973; *Chem. Gaz.* 1858, 64.
- On the formation of mixed acetones: by *C. Friedel*. *Compt. rend.* xlvii. 552; *Ann. Ch. Pharm.* cviii. 122.
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